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MUNICIPAL WASTEWATER ANAEROBIC TREATMENT WITH
ENHANCED CLARIFICATION

by

Kevin J. Berg

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Marquette University,
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ABSTRACT

MUNICIPAL WASTEWATER ANAEROBIC TREATMENT WITH ENHANCED CLARIFICATION

Kevin J. Berg

Marquette University, 2015

As energy costs rise, water reclamation facilities (WRFs) desire lower cost, easily operated systems to remove BOD₅ and suspended solids. WRFs typically utilize an aerobic process called activated sludge to remove biochemical oxygen demand (BOD). BOD, specifically 5 day BOD (BOD₅), is used as an indicator of the organic strength of a solution. Anaerobic treatment provides an alternative to activated sludge by removing BOD₅, generating biogas containing methane for energy and producing less biomass that requires disposal. Anaerobic treatment functions as an exceptional alternative to activated sludge when packaged as a system with a small footprint that operates at ambient temperature. These systems can produce effluent with organic constituent quality similar to activated sludge without requiring the energy inputs that conventional treatment demands.

In this work, an anaerobic, fluidized bed reactor (FBR) treating both synthetic and real domestic primary effluent was utilized to remove BOD₅ from wastewater. The reactor was operated at 10°C to determine operation under challenging, low-temperature conditions. An external, cross-flow tubular membrane, gravity settling, enhanced chemical coagulation, electrocoagulation and FBR treatment with no subsequent solids removal were all tested in an effort to increase effluent quality, targeting a final BOD₅ of 10 mg/L or less. FBR treatment with no subsequent solids removal with an hydraulic residence time of 9 hours reduced BOD₅ by 68%, from 199 ± 26 mg/L to 67 ± 15 mg/L (n=8). Clarification of anaerobic effluent by membrane filtration resulted in an average permeate BOD₅ of 7 ± 4 mg/L. Gravity settling alone achieved an average BOD₅ of 35 ± 5 mg/L (n=2). Chemical coagulation with 30 mg/L ferric chloride followed by gravity settling reduced the BOD₅ to 14 ± 5 mg/L (n=8). In comparison, full scale activated sludge with secondary settling achieved a final BOD₅ of 9 ± 2 mg/L (n=9).

Anaerobic treatment with enhanced sedimentation may lend itself to retrofitting existing plants by use of activated sludge tanks and existing secondary clarifiers, whereas membrane filtration requires large capital investment. Additionally, enhanced sedimentation is a robust and relatively simple process in comparison to membrane filter operation. Enhanced sedimentation is a viable option for clarification of anaerobic effluent from an anaerobic FBR treating primary effluent.

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Kevin J. Berg

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I would also like to thank my family for their support throughout my education. Whether the day was good or bad, they were always there for a conversation. For that, I will always be grateful. Thank you to everyone who helped to further my education and make this project a reality.

DEDICATION

This work is dedicated to my family and all who have helped me along the way, especially those who were not able to be here for its completion.

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1 INTRODUCTION

1.1 Research Motivation

Increased emphasis on reducing greenhouse gas emissions, rising energy costs and increasingly restrictive discharge permits combine to generate a need for advanced wastewater treatment technologies to reduce costs while maintaining regulatory compliance (EPA Office of Water, 2006). Traditionally, aerobic treatment (often activated sludge) is used to treat dilute effluent from the primary clarifier system. Difficulties and inefficiencies with transferring atmospheric oxygen into solution for microbial life make aerobic treatment energy intensive, consuming up to 50% of the total electricity used at a WRF (McCarty et al., 2011). Aerobic treatment removes organics from solution through biomass synthesis. Bacteria use the organics present in the wastewater as a food source by converting them into biomass, carbon dioxide and water, thereby removing the contaminant from solution. Aerobic bacteria have relatively high biomass yields that can generate large volumes of excess biomass requiring stabilization and disposal (Eckenfelder et al., 2009).

As an alternative to aerobic treatment, anaerobic treatment (AT) can be used to treat wastewater while generating useful byproducts like biogas. When combined with a tertiary nutrient recovery process like ion exchange, AT can also be a source of recovered fertilizer rich in nitrogen and phosphorus (Booker et al., 1999). Many anaerobic reactors are operated in the thermophilic (45-65°C) or mesophilic (25-45°C) temperature range. (Connaughton et al., 2006). These temperatures are far above wastewater temperatures in most climates, requiring heat to increase digester performance. Low temperature anaerobic treatment is an area of research that has been previously proven effective

provide that could prove to be cost effective use of anaerobic technology (Connaughton et al., 2006; Lettinga et al., 2001; Rebac et al., 1999; Smith et al., 2013).

This work had several main research goals, building upon previous work with cold temperature anaerobic treatment, fluidized bed reactors and clarification of anaerobic effluent. The term clarification is often used to describe sedimentation and gravity settling (Tchobanoglous et al., 2003). In this work, clarification is used as a catch-all term for solids removal by filtration, sedimentation or other means.

The project's main goals were as follows:

1. Demonstrate successful startup and operation of a cold temperature fluidized bed reactor treating synthetic and real primary effluent
2. Evaluate membrane filtration effluent (permeate) for quality relative to activated sludge effluent and typical permit requirements
3. Evaluate alternative options for reactor effluent clarification: gravity settling/sedimentation, enhanced sedimentation by addition of chemical coagulants, filtration by cloth media and electrocoagulation
4. Evaluate several coagulants and determine optimum coagulant and dose
5. Compare operational costs and chemical cost for the clarification options
6. Evaluate the effectiveness of a fluidized bed reactor system combined with clarification as a substitute for activated sludge

2 LITERATURE REVIEW

2.1 Wastewater Treatment

2.1.1 Wastewater Characteristics

Four different types of flows make up domestic wastewater: residential and commercial wastewater, industrial discharges, infiltration and inflow (I/I) and stormwater runoff (Tchobanoglous et al., 2003). Flow rates from these sources are based on many variables such as population density, neighborhood socioeconomic status, infrastructure condition, and regional climate (Reynolds and Richards, 1996).

Residential and commercial sources generate wastewater from locations such as houses, schools, and hotels. These areas discharge wastewater from both indoor and outdoor sources, including toilets, showers and sinks. On average, each person in the world uses between 9 and 24 gallons of water per day (Tchobanoglous et al., 2003). In comparison, a single person household in the United States uses between 80 and 100 gallons of water per person per day, with 60 to 90% becoming wastewater (USGS, 2014).

Industrial flows are typically more concentrated than residential or commercial wastewater, and sometimes contain high concentrations of metals, solvents, or other difficult to treat compounds. Sometimes industrial flows require pretreatment with an onsite treatment facility before discharge to the sewerage system. Industrial areas typically produce from 1,000 gallons per acre per day for light industry up to 250,000 gallons per acre per day for heavy industry (Reynolds and Richards, 1996). Between 85% and 95% of the water used onsite becomes wastewater if no internal recycling or reuse programs are followed (Tchobanoglous et al., 2003).

Inflow and infiltration refer to any liquid flow that makes its way into the sewer collection system through leaks in sewer piping or connections. These flows can be difficult to measure, but may significantly contribute to overall sewer flow, especially if infrastructure is in poor condition. Modern specifications call for limiting I/I to less than 500 gallons/(mile-day) per inch of pipe diameter (Reynolds and Richards, 1996). In addition to expected flows from domestic and industrial sources, I/I can be estimated between 30,000 and 60,000 gallons/(mile-day) depending on the region's soil type and groundwater elevation (Reynolds and Richards, 1996).

Domestic wastewater is collected and conveyed by either a combined or sanitary sewer system (Tchobanoglous et al., 2003). Combined systems convey all four sources of wastewater together in a single pipe. These systems may reduce the amount of buried piping, but require high flow capacities and can place stress on treatment facilities during rainfall events. The sanitary sewer is used to convey only sewage; a separate piping network collects conveys stormwater, which requires little or no treatment prior to discharge.

Modern engineering practice no longer includes design of combined sewer systems. Despite discontinuation of installation, these systems are currently in use from previously constructed projects. Combined sewers present challenges, particularly during rainfall events. As stormwater is added to the system, peak flow rates increase dramatically from dry weather conditions. Overflow storage capacity often must be included in order to store the combined sewage and stormwater until it can be treated following conclusion of the rainfall. If so much precipitation and runoff should occur so that the overflow facilities are at capacity, direct discharge of combined sewage occurs.

These discharges are harmful to the environment are not well regarded by the Environmental Protection Agency (EPA).

2.1.2 Treatment Regulations and Requirements

Since the 1970s, the United States has made significant advances in its regulation and control of wastewater discharge. In 1972, the Clean Water Act (CWA) established the National Pollution Discharge Elimination System (NPDES) permitting program, which formed the basis of discharge regulation as practiced today. The Water Quality Act (WQA), passed in 1987, strengthened these regulations and increased penalties for violations. Since the CWA and WQA, additional regulations have been passed concerning industrial wastewater discharges to sewerage systems, biosolids disposal, overflow policies and regulation, air quality requirements, and the total maximum daily load (TMDL) calculation system for receiving bodies of water (Tchobanoglous et al., 2003).

Since the CWA in 1972, all water reclamation facilities (WRFs) require secondary treatment prior to discharge. Definitions for secondary treatment can be found in public law PL 92-500 and its amendments. PL 92-500 defines minimum secondary treatment as having effluent with 30-day average concentrations of BOD₅ and TSS less than 30 mg/L, with pH between 6.0 and 9.0 at all times, although specific required discharge limits can be more stringent. Higher quality effluent may be required on a case-by-case basis depending on the receiving water body, but all secondary treatment in the United States must meet these minimum requirements. More recent regulatory changes have implemented the use of TMDL for discharge permits. TMDL-based regulation closely monitors the amount of pollutant (solids, organics, nutrients, etc.)

discharged to the environment, in an effort to protect and maintain existing water quality (Tchobanoglous et al., 2003). Pollutants may have a maximum concentration that can be discharged, but overall regulation is based on a mass loading delivered by the permit holder to the receiving body of water. TMDL regulation allows for some flexibility in the effluent quality without sacrificing the health of the receiving body of water.

2.1.3 Treatment Options

Federal and state regulation requires WRFs to consistently produce effluent that meets the terms of their discharge permits. In order to meet these, WRFs typically employ a two or three step process for wastewater treatment composed of primary, secondary and potentially tertiary treatment. An example of a traditional WRF employing these treatment steps is seen below in Figure 2.1.

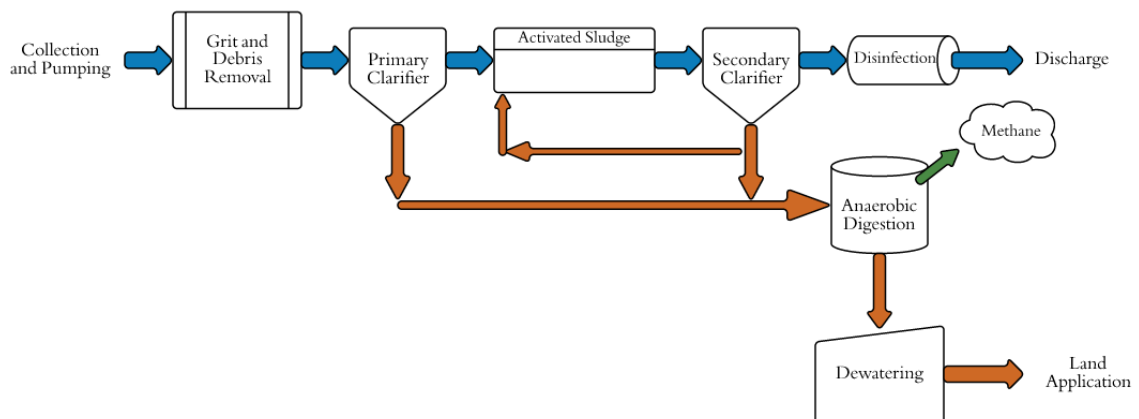


Figure 2.1: Conventional wastewater treatment plant with activated sludge

Primary treatment targets removal of solids and large debris, greatly lowering the demand on secondary treatment. Solids removal begins in primary treatment. Up to 50% of the BOD₅ entering the plant can be contained in the total suspended solids (TSS)

(Tchobanoglous et al., 2003). Effective primary treatment will remove a large percentage of those solids prior to secondary treatment. Removing solids is important in wastewater treatment since hydrolysis of particulate material is a relatively slow process.

Secondary treatment removes organics from the wastewater to levels below the discharge permit limit. In conventional plants this is often performed using activated sludge, which requires high energy inputs and generates large volumes of solids. Secondary treatment also requires solids stabilization. Anaerobic digestion is typically used to treat primary sludge and excess solids produced from activated sludge. Solids stabilization removes organic content from the concentrated solids flows, reduces the mass of volatile solids, and provides pathogen inactivation to allow for land application or other safe disposal of biosolids.

In addition to organic removal, secondary treatment often includes nutrient removal. Conventional plants may use activated sludge to perform nitrogen and phosphorus removal by way of nitrification/denitrification and biological phosphorus removal (bio-P), respectively (Tchobanoglous et al., 2003). Nitrification/denitrification converts ammonia into nitrogen gas, which then partitions to the atmosphere. Bio-P removes phosphate from solution through biological uptake and wasting of the biomass.

Tertiary treatment can include steps such as additional disinfection by chlorine or ultraviolet (UV) light or filtration by reverse osmosis (Reynolds and Richards, 1996). Ion exchange or struvite precipitation may be utilized to recover nitrogen and phosphorus to be used as fertilizer, rather than remove the nutrients and lose their potential benefits as wastes (Booker et al., 1999; Doyle and Parsons, 2002; Shu et al., 2006). Finally, post-

aeration prior to discharge may be required to meet dissolved oxygen (DO) requirements in the receiving water body (Tchobanoglous et al., 2003).

2.1.4 Energy and Costs

As energy costs rise, efficiency in energy intensive processes like wastewater treatment becomes a paramount concern and opportunity for innovation. In the United States, wastewater treatment accounts for about 3% of the total electrical load (EPA Office of Water, 2006). Estimates attribute about half of a WRF's electrical energy to activated sludge (McCarty et al., 2011). By those estimates, roughly 1.5% of the United States energy (~58 billion kWh/year) is utilized by activated sludge, an amount greater than the total yearly energy consumption of all but 43 countries in the world (CIA, 2015). Energy consumption in wastewater treatment is a major concern and has economic impacts on municipalities and rate payers.

Since 1990, the average of on and off peak electricity charges for large commercial customers in Wisconsin has nearly doubled, from \$0.02660/kWh to \$0.04491/kWh (Wisconsin Public Service, 2015a). Natural gas prices for large commercial customers increased 238% in the last 22 years, from an average value of \$0.2788 per therm in 1992 to \$0.6635 per therm in 2014 (Wisconsin Public Service, 2015b). These market trends directly increase costs associated with activated sludge treatment due to electrical demand for oxygen transferring equipment and solids handling and stabilization.

Evaluation of anaerobic systems as energy efficient secondary treatment systems has been shown to be possible and practical (Huang et al., 2008; McCarty et al., 2011; Seghezze et al., 1998; Shin et al., 2014; Smith et al., 2012). Speece (1983) estimated that

anaerobic systems may be able to operate at a \$160 discount compared to aerobic process when normalized to one metric ton of COD destroyed for concentrated wastewater. Most anaerobic systems require heating to around 35°C, which is commonly supplied by natural gas or biogas. From a purely economic standpoint, anaerobic treatment at ambient temperatures provides a cost-saving treatment option in terms of electricity, natural gas, and solids disposal.

2.2 Anaerobic Treatment

2.2.1 Theory and Function

Anaerobic digestion (AD) is a well-established, extensively studied, and commonly employed treatment process at WRFs (McCarty and Smith, 1986). AD is the breakdown of organic matter to methane, carbon dioxide and water (Speece, 1983). Biogas, which contains methane, is the target byproduct and can be burned to fuel generators, boilers, or other systems that utilize natural gas as a fuel source.

AD is a biological process and is dependent on several groups of microbes to complete the overall reaction. Each group carries out a portion of the reaction, which serves to further the entire process. AD can be separated into four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (McCarty and Smith, 1986; Rittman and McCarty, 2001; Speece, 2008). These steps must be carried out in concert for the process to function effectively. If any of the steps is out of synchronization with the others, the environment can become unfavorable to a portion of the biological community and the process will be inhibited or will fail.

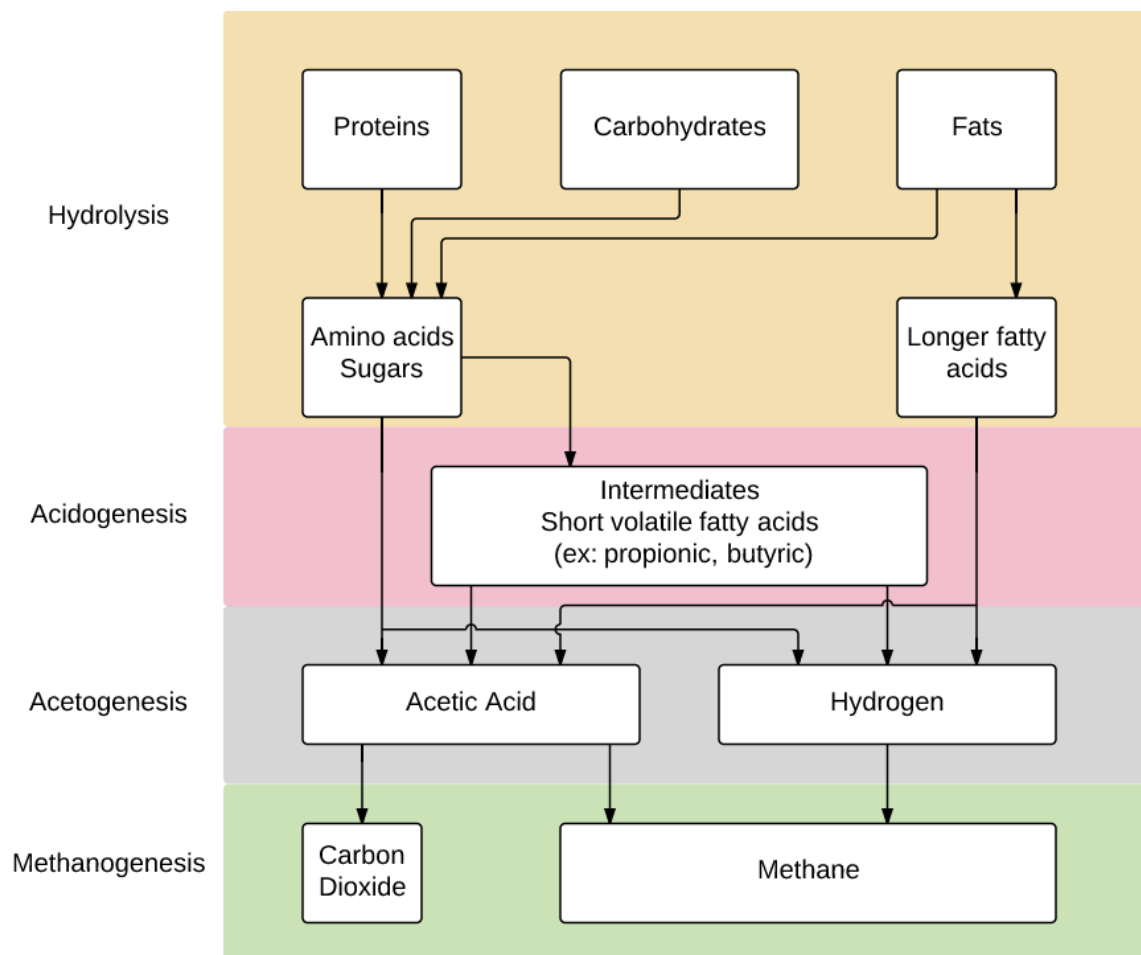


Figure 2.2: Organic pathways through anaerobic treatment and methane generation

Hydrolysis is carried out by many different microbes, most classified as chemoheterotrophs, or microbes that get their energy from chemicals and use organics as their carbon source (Madigan, 2012; Speece, 1983). Large, particulate compounds are broken down and hydrolyzed to smaller, soluble compounds in this step. Through several steps, most of the complex matter is degraded to long chain, volatile fatty acids (VFAs) such as valyric, butyric and propionic acid (Speece, 1983).

In acidogenesis, bacteria convert simplified carbohydrates, proteins and acids to hydrogen gas and shorter VFAs such as isobutyric, n-butyric, propionic, and acetic acids (Rittman and McCarty, 2001). These VFAs are typically in the greatest abundance in a

digester and serve as important indicators of process health and efficiency. A smaller fraction of the particulate matter is degraded directly to acetic acid or hydrogen gas.

Following hydrolysis and fermentation, acetogenesis is the oxidation of the long chain VFAs to acetate and hydrogen gas. This step is very important and is directly linked to methanogenesis due to the required interaction between the methanogens and the acetogens. Acetogenesis is particularly important to the methanogenic community, as acetate and hydrogen gas serve as the two main substrates for methanogens (Rittman and McCarty, 2001). These two groups exist in a symbiotic relationship and typically control reactor design due to their relatively slow growth and susceptibility to various toxicants.

Concurrent with acetogenesis, methanogenesis is carried out by Archaea that produce methane in a strictly anaerobic environment. Three main substrates are used in methanogenesis: carbon dioxide, methylated substrates, and acetate (Madigan, 2012). Carbon dioxide (CO_2), formate (HCOO^-), and carbon monoxide (CO) are reduced to methane (CH_4) through the use of hydrogen gas (H_2) as the electron acceptor. Methylated structures like methanol (CH_3OH) or methylmercaptan (CH_3SH) are reduced to methane through a similar pathway that utilizes H_2 as the electron acceptor. Finally, methane is produced directly from acetate, resulting in CO_2 and CH_4 .

The energy yield from the hydrolysis and acidogenesis reactions is relatively high in comparison to acetogenesis or methanogenesis, allowing for faster growth rates when compared to the other steps. Thus, the hydrolysis step typically is not rate-limiting, except in instances where very complex cellulosic substrate is present (Rittman and McCarty, 2001). In the case of complex wastewaters, hydrolysis may control at low

organic loading rates. As the loading rate increases, VFA production may increase to a point where methane production begins to control the process (Speece, 1983).

2.2.2 Methanogens

Methanogens are part of the *Archaea* domain, and are inhibited by several common toxicants, most notably oxygen. In addition to oxygen sensitivity, methanogens grow best at neutral pH (6.5-7.6) and at temperatures between 15°C and 100°C (Rittman and McCarty, 2001). Despite this wide temperature range, most methanogens are mesophilic or thermophilic with optimum growth rates around 35°C or 50°C, respectively. In addition to mesophilic or thermophilic digestion, psychrophilic (2-20°C) methanogenesis has also been studied and utilized to treat a variety of wastes (Connaughton et al., 2006; Lettinga et al., 2001; Rebac et al., 1999; Shin et al., 2014; Smith et al., 2013; Yoo et al., 2014).

The two common groups of methanogens are referred to as hydrogenotrophic and acetoclastic methanogens. As the name suggest, hydrogenotrophic methanogens utilize hydrogen gas and carbon dioxide based compounds to produce methane, whereas acetoclastic methanogens utilize acetate to produce methane. In general, hydrogenotrophic methanogens are more common than acetoclastic methanogens (Madigan, 2012).

2.2.3 Digester Configurations

Anaerobic digesters for solids stabilization are routinely operated as completely mixed, stirred-tank reactors (CSTRs). These types of reactors are usually found as either pancake or egg style digesters. As the names suggest, pancake type digesters are

cylindrical, with diameters that are typically much greater than their height. Egg shaped digesters use an upright, oblong shape to promote mixing. Proper mixing is essential to AD to provide contact between the active microbes and the substrate in the bulk liquid.

CSTRs are commonly operated as mesophilic or thermophilic, each with benefits and shortfalls. Thermophilic treatment is most commonly employed to provide pathogen removal in order to produce Class A biosolids (Speece, 2008). Increased heat inputs, increased heat losses, and operating concerns with elevated VFA production are all associated disadvantages with thermophilic treatment. Mesophilic digesters have been more commonly employed due to more stable operation and lower heating inputs.

Two primary design considerations with AD reactors are hydraulic residence time (HRT) and solids retention time (SRT). These terms correspond to the average time a volume of water or solids spends in the reactor, respectively. The HRT and SRT of a CSTR are equal, due to the ideal assumption that its contents are well-mixed. A well-mixed digester contributes both positive and negative characteristics with regards to its treatment capabilities. Adequate mixing provides good microbe to substrate contact, enabling active biomass to perform well and degrade organics. In contrast, a well-mixed environment also causes active biomass to be lost in liquid leaving the reactor. Therefore, CSTRs must maintain a relatively high HRT, which translates to relatively large reactor volumes, in order to prevent washout. Washout will occur when the HRT of a CSTR is lower than the growth period of a microbe to maintain a functional population (Tchobanoglous et al., 2003).

Separation of the HRT and SRT in a digester can provide many functional advantages over a CSTR. Most notably, dramatic reductions in reactor volume can be

achieved while maintaining comparable levels of treatment. Reactor configurations that allow for separation of the HRT and SRT include the upflow anaerobic sludge blanket (UASB), expanded granular sludge bed (EGSB) reactor, and the fluidized bed reactor (FBR).

Reactors with separated HRT and SRT parameters exhibit many benefits aside from reduced tank volumes. These reactors can usually operate with higher organic loading rates and at lower temperatures than comparable CSTR systems. Additionally, these types of reactors are applicable to a wide range of process flow volumes, making them useful for WRFs of varying sizes (Seghezzo et al., 1998).

UASB reactors have been utilized in tropical and subtropical climates for secondary treatment with good to fair success (Foresti et al., 2006). These reactors require development of a sludge layer that does not easily washout. Development of this layer can be difficult to control and often requires a long startup period (Seghezzo et al., 1998). In contrast, EGSB and FBR setups can utilize a media that remains in the system that promotes biomass attachment and growth. Even with the use of an attached growth media, microbes and solids are included in reactor effluent, potentially causing the effluent to not meet permit requirements. Clarification of reactor effluent can be performed to remove solids and BOD₅ to meet permit expectations.

Attached growth reactors like UASB, EGSB or FBR reactors gain operational efficiency through increased mass-transfer kinetics at the biological level (McCarty and Smith, 1986). Specifically, the syntrophic relationship between bacteria performing acidogenesis, acetogenesis and methanogenesis is maximized when the bacteria are close

to each other. These types of reactors promote close-proximity growth which enables high mass transfer rates, which allows for high treatment efficiencies.

2.3 Clarification of Anaerobic Effluent

2.3.1 Membrane Coupled Anaerobic Systems

In an effort to promote biomass retention while producing high quality effluent from reactors, external and submerged membrane units have been used to filter anaerobic effluent (Dereli et al., 2012; Kim et al., 2011; Skouteris et al., 2012; Smith et al., 2012; Stuckey, 2012). These systems are capable of generating very high quality permeate, and have been of recent interest (Kim et al., 2011; Shin et al., 2014; Smith et al., 2013). As an added benefit of removing solids from the effluent stream to meet permit regulations, the retained biomass is kept in the system to perform treatment in the bulk liquid.

Membrane pore sizes typically provide micro- or ultrafiltration (Smith et al., 2012). The units are typically located and operated as either external cross-flow, internal submerged, or external submerged (Smith et al., 2012). Crossflow style membranes utilize positive pressure to create permeate by pushing wastewater through the membrane material. Submerged membranes utilize vacuum applied to the membrane to pull liquid through the membrane surface. Retentate from all systems is returned to either the bioreactor or the tank in which the membrane is housed in the case of an external submerged membrane system.

Membrane filtration for anaerobic effluent has been applied to many reactor configurations, including CSTR (Smith et al., 2013) and attached growth style reactors (Hu and Stuckey, 2006; Kim et al., 2011; Shin et al., 2014). Anaerobic treatment and

membrane filtration produced quality effluent ($\text{BOD} \leq 30 \text{ mg/L}$), even at low temperatures (Shin et al., 2014; Smith et al., 2013). Despite its advantages for effluent clarification, membrane filtration comes with several operation concerns.

In addition to high initial cost, membrane design and operation can be difficult. Both operation and design require estimation and monitoring of several parameters critical to operation. Membrane flux is the rate of flow through a unit area of membrane surface. This value is critical to design as it will drive both membrane sizing and cleaning frequency. If a crossflow system is used, the velocity of the liquid as it passes through the membrane is an essential design input for both financial estimation of pumping costs as well as estimating the fouling rate of the membrane. Membrane life, initial price and flux capabilities are key design parameters to evaluate the feasibility of a membrane-coupled system for wastewater treatment (Lin et al., 2011).

Even as membrane technology advances and becomes less cost prohibitive, capital costs of membrane implementation remain high. Implementing a membrane system has limited economy of scale until daily flow reaches about $2500 \text{ m}^3/\text{day}$. At design flows of $2500 \text{ m}^3/\text{day}$ and above, costs stabilize at about $\$1000/\text{m}^3$ treated-day. The membrane units make up nearly 75% of this cost. These costs translate to capital costs of around $\$378,000,000$ for a 100 MGD ($378,000 \text{ m}^3/\text{day}$) plant to incorporate a submerged, anaerobic membrane system (Lin et al., 2011).

A fluidized bed reactor with effluent clarification by a method other than membrane filtration to provide permit quality effluent has not been heavily researched. A full scale UASB plant treating domestic sewage in India achieved BOD removal of 75%, but was not able to meet permit requirements (30 mg/L BOD and 50 mg/L TSS) thus

requiring post treatment (Draaijer et al., 1992). Post treatment options were not discussed, but a larger UASB plant in Mirzapur, India was referenced. The Mirzapur facility uses gravity settling in a high rate oxidation pond with a 1-day retention time to clarify anaerobic effluent (Draaijer et al., 1992). Treated effluent from the pond was used mostly for irrigation (NIIR, 2005).

Lack of research applying clarification to anaerobic effluent is likely due to the typical use of anaerobic digestion in conventional treatment plants. Digester effluent is usually sent to solids disposal or dewatering, where equipment such as gravity belt thickeners or centrifugal separators are used in place of clarifiers. Clarifiers are usually used to settle aerobic effluent from the activated sludge process (Tchobanoglous et al., 2003).

2.3.2 Chemically Enhanced Sedimentation

Sedimentation has long been used in wastewater treatment and can be used to remove both suspended and colloidal material (Tchobanoglous et al., 2003). In its simplest form, gravity sedimentation removes particles with a high specific gravity with very little design requirement. The only necessity for this type of work is tankage with low velocity gradients and a method for removal and disposal of the settled sludge. Sedimentation is an essential unit process in the wastewater treatment chain, providing removal of suspended organics in primary treatment, as well as allowing for the return of beneficial biomass in the treatment chain during secondary treatment.

Sedimentation as a unit process is first employed in the grit chambers and primary settling tanks of a WRF. Grit chambers provide removal of sand, gravel, or other materials with a specific gravity much higher than that of other organic materials in

wastewater. Primary clarifiers follow the grit chambers and target readily settleable solids. The solids removed from suspension can contain 50-70% of the TSS and 25-40% of the BOD₅ of the incoming wastewater (Tchobanoglous et al., 2003). Sedimentation plays an important role in separating solids from the liquid stream which reduces the organic content of the primary effluent (PE), enabling secondary treatment to reach very low levels of TSS and BOD₅.

Typical primary clarifiers have a detention time of 1.5-2.5 hours. A short HRT allows for small tank volumes, reducing capital cost and land requirement. Increasing the HRT of these tanks beyond three hours provides marginal increases in TSS and BOD₅ removal, while requiring large increases in tank volumes (Tchobanoglous et al., 2003). Increasing or maintaining the efficiency of a primary clarifier usually can be linked to maintaining even, low velocity flow throughout the clarifier. Flow gradients can often be attributed to poor influent flow dispersion, wind over the surface of the clarifier, or temperature gradients in the clarifier. All of these issues reduce the efficiency of the clarifier, generating higher TSS and BOD₅ concentration in the clarifier effluent.

Addition of a chemical coagulant can improve clarifier function and increase process efficiency. Coagulation is a chemical process that encourages small, colloidal particles to group together, forming larger particles (Reynolds and Richards, 1996). These colloidal particles do not settle within a reasonable amount of time under the effects of gravity alone. Addition of a metal salt such as alum ($[\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}]$) or ferric chloride (FeCl_3) is commonly used in wastewater treatment to provide coagulation for removal of colloidal materials (Reynolds and Richards, 1996; Tchobanoglous et al., 2003).

Coagulants work by destabilizing the surface charge of colloidal particles (Reynolds and Richards, 1996). These small particles typically have like surface charges and therefore repel each other. Destabilization of the surface charge allows for these colloids to merge together and form large particles. The larger particles can then be settled out of solution. The large particles generated by the colloidal materials are called flocs. Flocs pick up more material by either charge attraction or enmeshment of other particles. Charge attraction draws material with opposite charges, while enmeshment gathers more material in the floc by physical entrapment.

Coagulants are sometimes used in primary and secondary settling chambers, and have been well developed and researched since the 1970s (Parker et al., 2001). Chemically enhanced primary treatment (CEPT) has been researched and tested as an alternative to biological treatment for organic and nutrient removal, but has demonstrated mixed results in generating the targeted effluent. Despite shortfalls in effluent quality, a major conclusion has been that by enhancing the treatment abilities of the primary settlers, demands on downstream treatment processes are lessened in terms of organic and nutrient removal.

As an alternative to chemical addition, electrocoagulation has been used to treat wastewaters as well as anaerobic effluent (Gengec and Kobya, 2013; Khoufi et al., 2006; Xu and Zhu, 2004). This process produces charge destabilization and flocculation similar to chemical coagulation without the addition of chemical coagulants. Direct current is passed between iron or aluminum cathode and anode plates, causing the release of the respective metal ions. Flocculation and sedimentation of colloidal and particulate material proceeds similarly to chemical coagulation.

2.4 Research Needs

Currently, WRFs require a treatment regime that is energy-efficient, stable, and produces a high quality effluent at the lowest cost possible. These constraints have been met for decades at conventional facilities utilizing activated sludge, clarification and nutrient removal processes. As energy costs, population, regulation and demands on WRF all rise, an alternative to activated sludge could be very beneficial to treatment facilities around the world.

In order to provide a sustainable treatment system, a reorganization of the unit processes available to WRF designers may be most beneficial. Anaerobic reactors such as UASB or FBR have been shown to work effectively to reduce organic and solids concentrations in a low footprint configuration in warm, tropical climates. CEPT effectively reduces loadings to downstream processes, allowing for smaller WRFs or increases in capacity by reducing HRT in existing tanks. Clarification of anaerobic effluent can produce a quality effluent rich in nutrients that can be recovered, rather than lost to the atmosphere or biosolids (Mullen, 2015; Williams, 2013)

A combination of these techniques leads to an experimental design of an anaerobic, attached growth reactor treating PE. Clarification of reactor effluent should be evaluated by many existing systems that could easily be implemented by a WRF. These systems should include gravity settling, enhanced settling similar to CEPT, and membrane filtration. Finally, one key to energy savings with an anaerobic system is reduction or elimination of heating costs. Therefore, to maximize the cost savings and efficiency of this system, testing at a low temperature representative of a temperate climate would yield beneficial results.

In this work, an anaerobic FBR reactor was operated at ambient temperature for a cold-weather temperate climate (10°C). Successful startup and continued operation of the fluidized bed reactor at cold temperatures was a major goal of this project. Additionally, operation of this reactor utilizing real wastewater was a key factor in determining its application to pilot or full scale use. As such, the reactor was first fed synthetic wastewater, then switched to real PE from a local WRF.

Over the course of the project, several clarification techniques were applied to the reactor effluent over the timeframe it was fed real PE effluent. Clarification refers to any process that further reduces TSS or organic concentrations in the liquid. In this work it applies to membrane filtration, sedimentation, enhanced sedimentation and others. Membrane ultrafiltration was utilized for the majority of the project, then removed in order to test alternate clarification methods. Also evaluated were gravity settling, chemical coagulation, a large opening cloth filter, and electrocoagulation. Comparison of clarification techniques was based on TSS and BOD₅ concentrations. The data obtained in this study may be useful for evaluation and implementation of a cold temperature anaerobic technology that produces effluent with similar quality to activated sludge.

Evaluation of clarification methods other than membrane filtration may provide a treatment technology that is more cost effective and less operationally challenging. A paradigm shift from aerobic to anaerobic secondary wastewater treatment may yield energy and economic savings, while producing beneficial products like biogas and fertilizers.

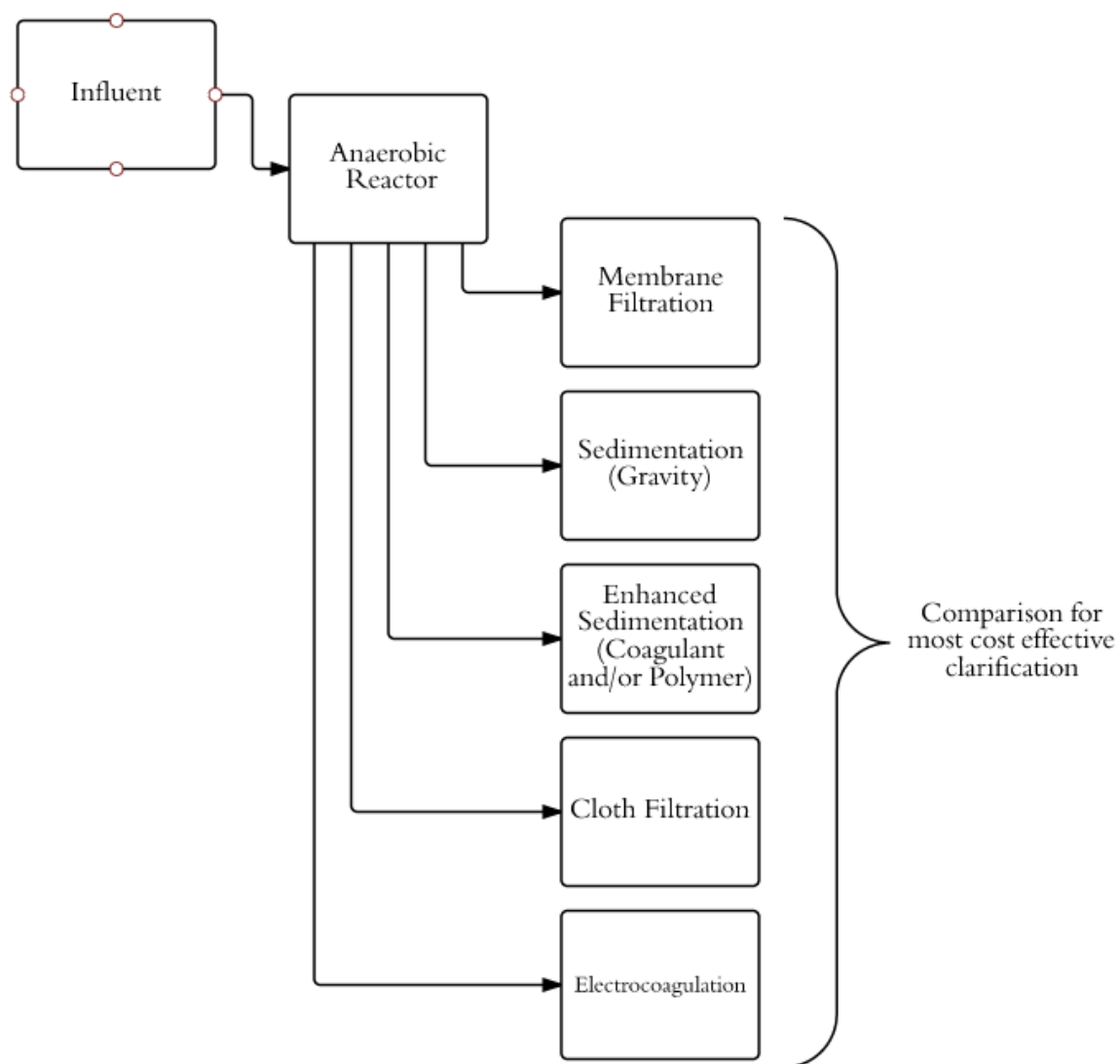


Figure 2.3: Project plan including anaerobic treatment and clarification methods evaluated

3 MATERIALS AND METHODS

3.1 Experimental Design

3.1.1 System Overview

An upflow, fluidized bed reactor (FBR) was constructed to treat municipal, PE (Figure 3.1). The bed material was granular activated carbon (GAC), fluidized to 200% of its original volume. Effluent from the reactor was treated by membrane filtration, gravity settling, enhanced sedimentation and electrocoagulation. In order to provide consistent flow to the membrane unit, a flow equalization tank (EQT) was used to collect and distribute flows from the reactor and to the membrane unit. Overall, the system liquid volume was 3.2 L. Influent was stored in a well-mixed, 20 L glass carboy. The entire system was enclosed in a refrigerator maintained at 10°C (StableTemp, Cole Parmer, Vernon Hills, Illinois). Peristaltic pumps (Masterflex, Cole Parmer, Vernon Hills, Illinois) were used to convey flow.

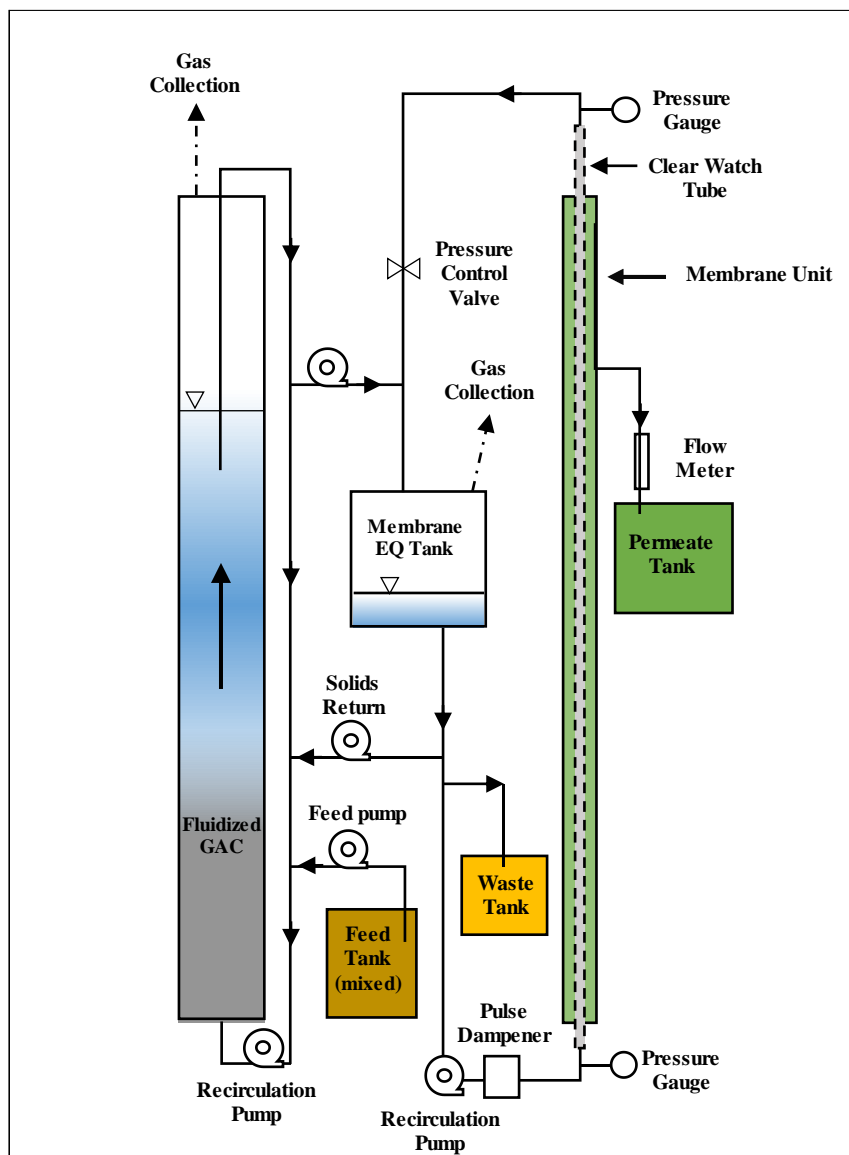


Figure 3.1: Schematic of upflow system showing reactor and tank arrangement with process flow indicators

3.1.2 Reactor Setup

A bench-scale, anaerobic reactor was constructed from clear polyvinyl chloride (PVC) piping. The reactor was nominally 2.5 inches in diameter, 39 inches long, and had a working volume of 2.2 L. A union joint was placed at a height of 28 inches to allow access to the contents of the reactor. A drop tube was submerged approximately six

inches into the bulk liquid to allow for recycle flow. A flow distributor was attached to the lower inlet to promote even flow through the GAC bed. Upflow velocity in the reactor was 30 meters per hour. Norprene tubing was used to convey all process flows.

3.2 Reactor Operation

3.2.1 Reactor Seeding

Each bioreactor was inoculated with 2 g VSS of a biomass mix from five sources: (1) mesophilic upflow anaerobic sludge blanket (UASB) reactor 1 treating brewery wastewater, (2) UASB reactor 2 treating brewery wastewater, (3) a mesophilic municipal anaerobic digester treating primary and waste activated sludges, (4) an ambient-temperature industrial anaerobic lagoon treating sugar beet waste, and (5) a laboratory, mesophilic anaerobic propionate enrichment culture previously described by Tale et al. (2011) and Bocher et al. (2015).

3.2.2 Reactor Feed

The reactor was fed synthetic feed from Day 0 to Day 323 of operation. The synthetic feed was a mixture of complex organic substrates and metal salts formulated to replicate PE at South Shore Water Reclamation Facility (SSWRF) (Milwaukee, WI) as shown in Table 3.1. Initial testing was conducted to determine characteristics of the wastewater related to organic content, solids, nutrient, and metals concentrations. The synthetic feed was prepared daily by diluting an appropriate volume of concentrated organic compounds solution, salt solution, metals solution and alkalinity with 20 L of deionized water. The concentrated organics solution contained powdered milk, casein

peptone, yeast extract, sodium acetate, starch, and cysteine. Salts, metals, and alkalinity were stored separately at 4°C to prevent chemical or biological degradation.

Table 3.1: Synthetic feed constituents and concentrations

Constituent	Manufacturer	Location	Concentration (mg/L)
Sodium bicarbonate	BDH / VWR	Radnor, PA	510
Calcium chloride dihydrate	Amresco	Solon, OH	275
Magnesium chloride hexahydrate	Amresco	Solon, OH	260
Sodium chloride	BDH / VWR	Radnor, PA	140
Instant, non-fat dry milk	Roundy's Supermarkets	Milwaukee, WI	133
Soluble potato starch powder	JT Baker	Center Valley, PA	133
Sodium acetate trihydrate	Amresco	Solon, OH	75
Casein peptone	Alfa Aesar	Ward Hill, MA	67
BBL Autolyzed yeast cell extract	Becton, Dickinson and Company	Erembodegem, Belgium	67
Ammonium chloride	BDH / VWR	Radnor, PA	64
Magnesium sulfate	BDH / VWR	Radnor, PA	36
Iron(II) sulfate heptahydrate	Amresco	Solon, OH	23
Potassium chloride	BDH / VWR	Radnor, PA	12
L-cysteine, 97%	Aldrich	St. Louis, MO	10
Potassium iodide	BDH / VWR	Radnor, PA	10
Magnesium hydrogen phosphate trihydrate	Alfa Aesar	Ward Hill, MA	7
Sodium hexametaphosphate	Acros	New Jersey, USA	4
Cobalt(II) chloride hexahydrate	Mallinckrodt	Paris, KY	1
Nickel(II) chloride hexahydrate	Fisher Scientific	Fair Lawn, NJ	1
Zinc(II) chloride	Alfa Aesar	Ward Hill, MA	1
Aluminum(II) chloride hexahydrate	Alfa Aesar	Ward Hill, MA	0.5
Ammonium metavanadate	Alfa Aesar	Ward Hill, MA	0.5
Boric acid	BDH / VWR	Radnor, PA	0.5
Copper(II) chloride dihydrate	Amresco	Solon, OH	0.5
Manganese(II) chloride tetrahydrate	JT Baker	Phillipsburg, NJ	0.5
Sodium molybdate dihydrate	Alfa Aesar	Ward Hill, MA	0.5
Sodium selenite	Aldrich	Milwaukee, WI	0.5
Sodium tungstate	Alfa Aesar	Ward Hill, MA	0.5

Real PE wastewater was collected from SSWRF weekly and subsequently stored at 4°C until use. PE was collected in 100-gallon batches, separated into two 55-gallon drums. PE was gathered from the effluent trough at SSWRF following primary treatment. Liquid was pumped from the trough using a portable electric pump. Following collection, PE was fed to the system using the same well mixed carboy setup used for synthetic wastewater.

3.2.3 Daily Operation

The reactor was operated in a continuous feed mode. Some anaerobic effluent was diverted from the membrane, since the membrane was not sized to process all of the bioreactor flow under all conditions. This excess flow was collected and quantified in terms of solids and COD. The initial hydraulic retention time (HRT) of the reactor was 12 hours, which was subsequently reduced to 9 hours after the operating temperature was reduced to 10°C as described below. The organic loading rate (OLR) of the reactor was nominally 2 g COD/(L-day) during feeding of synthetic wastewater. After switching to real PE wastewater, the OLR fluctuated based on the variability of the PE wastewater batches collected, resulting in a lower average OLR of 1.3 g COD/(L-day).

3.2.4 Biogas Collection and Methane Measurement

An impermeable gas collection bag (Tedlar® sampling bag, Environmental Sampling Supply, San Leandro, California) was attached to the top of each reactor and EQ tank to collect biogas. Biogas production was measured by detaching the bag from the reactor and withdrawing the biogas with a 140 mL syringe. Volume measurements were made at 10°C.

Samples were collected from the biogas bag for methane content. Methane content in the biogas was measured by gas chromatography (7890A, Agilent, Palo Alto, California) with a thermal conductivity detector (TCD). The carrier gas was helium at 30 mL/min. Injector, oven, and detector temperatures were 40°C, 120°C, and 250°C, respectively.

3.3 External Membrane

A ceramic, hollow tube membrane with a nominal pore size opening of 20,000 Daltons (20 kDa) was used to clarify anaerobic effluent. The membrane was contained in a stainless steel housing. The housing collected permeate in a jacket around the membrane, with a holdup volume of approximately 250 mL. The housing had both upper and lower ports to allow permeate to exit the jacket. Permeate was allowed to flow by gravity from the upper port. Pressure gauges were installed on both ends of the membrane, allowing calculation of the average transmembrane pressure (TMP).

Membrane operation was based upon a constant flux, variable TMP methodology. As shown in Figure 3.1, the TMP could be increased by restricting flow through the tubing connecting the membrane housing to the EQ tank. Flux rate was monitored by a variable area flow meter and held constant at 7.4 L/m²-hr. Crossflow velocity through the membrane was 0.27 m/s.

Membranes were considered fouled when the average TMP increased above 0.9 bar. Once a membrane fouled, it was removed and cleaned by spraying the inside of the membrane tube with a water jet to remove the fouling cake layer then chemically cleaned by soaking in a high pH bath for 60 minutes and then with an acidic bath for 25 minutes. For the ceramic membrane, the high pH bath consisted of a solution of NaClO (200 ppm free chlorine) adjusted to a pH of 11 using 6N NaOH. For the polymeric membrane, the high pH bath consisted of a solution of NaClO (200 ppm free chlorine) with a pH of 10. The acidic bath for both membranes consisted of distilled water adjusted to a pH of 2 using HNO₃.

3.4 Chemical Coagulation

3.4.1 Batch Testing

Anaerobic effluent from the bioreactor was collected as a 24 hour composite sample at 10°C. Sample was allowed to continuously flow from the reactor by gravity into the collection vessel over the 24-hour period. Following collection, the sample was tested for pH, total solids, volatile solids, total suspended solids, volatile suspended solids, total COD, soluble COD, and turbidity. Any portion of the sample that was not immediately used was stored at 4°C, and was used within 24 hours for testing. The same set of analyses were run on the supernatant in each jar following coagulation, flocculation and settling. All analyses were conducted according to standard methods (APHA et al., 1999)

Batch tests were conducted utilizing a six-jar gang mixer (Model 7790-400, Phipps and Bird, Richmond, Virginia) . One liter of effluent was added to each jar, and mixed at 70 rpm. Coagulant and/or polymer was then dosed. The polymer was Clarifloc C-342 (Polydyne, Riceboro, GA). Both alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, Sargent Welch, Skokie, IL) and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Mallinckrodt Chemical, Phillipburg, NJ) were prepared in stock solutions (10 g/L) and stored in the dark at 4°C. Additives were rapidly mixed (70 rpm) with the effluent for a period of one minute, flocculated at three rpm for three minutes, and then allowed to settle for 60 minutes. Mixing times were determined experimentally. Supernatant was withdrawn using a pipette from a distance of approximately 0.5 inches under the surface to avoid any floating particles. Supernatant was collected after 10, 30 and 60 minutes of settling, taking care to avoid the floating

layer. Solids analysis was performed only on the anaerobic effluent and supernatant at sixty minutes of settling.

3.4.2 Cloth Media Filtration

A 20 L composite sample of anaerobic effluent was filtered through a proprietary cloth media filter (OptiFiber, Aqua-Aerobic Systems, Rockford, IL) with a nominal pore size opening of 10 microns. The sample was filtered using a bench-top apparatus supplied by the cloth media manufacturer. Filtrate was collected and tested for TSS and BOD₅ concentrations. Both primary effluent and anaerobic effluent were treated using the cloth filter.

3.4.3 Electrocoagulation

Electrocoagulation was tested as an alternative to chemical coagulation to avoid the costs of transporting, storing, and implementing chemical coagulants. This process produces charge destabilization and flocculation similar to chemical coagulation without the addition of chemical coagulants.

Preliminary testing with electrocoagulation was conducted utilizing a lab-scale setup (Heffron, 2015). Operating conditions included a 300 mL reactor volume, 0.5 amp direct current, 9 volts, and reaction time of one minute. In order to provide adequate sample volume, six treated batches were combined in a two liter beaker following electrocoagulation treatment. This composite sample was then slowly mixed at 3 rpm for 3 minutes then settled for 60 minutes.

3.4.4 Cost Analysis of Clarification Options

A hypothetical plant treating 100 MGD of low strength wastewater was utilized to evaluate all treatment options. Membrane filtration costs were estimated using values generated by unpublished research by Seib et al. (2015). Electricity costs were estimated using historical electrical rates for large industrial users compiled by the Wisconsin Rate Book (2015a). Chemical coagulant costs were sourced from industry representatives and appear in Table 3.2. In addition to coagulant costs, electricity usage for operation of a secondary clarifier for a 100 MGD plant was obtained from Newell et al. (2012).

Electricity usage estimates from this work were combined with current rates from the Wisconsin Rate Book to create an operating cost per 1000 m³ treated for a secondary clarifier system. This price equated to \$2.38 per 1000 m³ treated and was added to all optimum dose prices. Solids disposal costs were not included for any clarification method, since they were assumed to be equal for all methods and outside the scope of this work.

Table 3.2: Summary of chemical costs used for enhanced sedimentation with sources

Chemical	Chemical Cost (USD per ton)	Date Obtained	Source
Ferric chloride	\$485	January 2015	City of Rochester, Minnesota
Alum	\$489	January 2015	City of Rochester, Minnesota
Cationic polymer	~\$200	January 2015	Polydyne – SNF Holdings Corp. (Riceboro, GA)
Hydrochloric acid	\$212 (22% solution)	February 2015	Qwest Chemical (Menomonee Falls, WI)
Sodium hydroxide	\$250 (50% solution)	February 2015	Qwest Chemical (Menomonee Falls, WI)

3.4.5 Sequential Filtration for COD Separation

Cellulosic membrane disc filters (Millipore) were used to determine size fraction of COD in PE and anaerobic effluent. A series of filters (3.0, 1.2, 0.8, 0.45, and 0.22 microns) was used. A vacuum driven, 47 mm membrane disk filtration system was used to filter samples. The system consisted of a magnetic filter holder funnel (Part 4247, Pall Corporation, Cortland, New York) attached to a 250 mL vacuum flask. The system was powered by a vacuum pump (Model 2545B-01, Welch, Niles, Illinois) regulated to 10 psig vacuum pressure. Sample was applied until the filter was fouled and could not process additional sample. Filtrate was collected in a clean vial and immediately analyzed for total COD concentration. Filters were not reused and the apparatus was rinsed between each use. Filtering was not sequential, meaning that unfiltered sample was applied to each filter during every test.

3.5 Analytical Methods

3.5.1 Standard Methods

Standard methods were used for the following analyses: COD, BOD₅, turbidity, total nitrogen, total phosphorus, total solids, volatile solids, total suspended solids, and total volatile solids. Total dissolved solids was computed as the difference between total solids and total suspended solids. Turbidity was measured using a turbidimeter (2100AN, Hach, Loveland, CO) calibrated with Hach StablCal® formazin standards. The pH was measured using a probe (Orion 4-Star pH, Thermo-Scientific, Waltham, Massachusetts).

Throughout the project, soluble COD (SCOD) was measured in influent, reactor contents, membrane retentate and membrane permeate. SCOD was also measured before and after treatment using enhanced sedimentation. Additionally, bioreactor contents were sampled and analyzed for BOD₅ while treating real PE. SCOD concentration was measured by first filtering the sample through 0.45 micron cellulose nitrate filters (Millipore, Billerica, Massachusetts), then analyzing the filtrate for COD concentration. Early variability in the influent SCOD concentration was attributed to sensitivity in the COD detection method and is explained below.

Low concentration (10-100 mg/L COD) solution was used in COD analysis from the start of the project until approximately day 150. This method required 1:10 dilution of the samples, resulting in high variability. Following day 150, high range COD solution (100-1000 mg/L) was used for analysis. This solution did not require dilution, resulting in decreased variability.

3.6 Statistical Analysis

Statistical analysis was performed using the GraphPad Prism® software package. Standard deviation was calculated when at least 3 results were available. Statistical significance was evaluated using Student's t test. Significance indicated by a p-value of less than 0.05.

4 RESULTS AND DISCUSSION

4.1 Reactor Performance

4.1.1 Startup and Stability

Reactor startup was successful, with continued operation for 383 days. The project proceeded in accordance with the timeline presented in Table 4.1. Major milestones included project startup, system refrigeration to 10°C, HRT reduction, conclusion of membrane filtering, and testing of various clarification techniques.

Table 4.1: Project timeline with major occurrences

Date	Day of Operation	Action
March 18, 2014	0	Reactor startup at room temperature
May 2014	45	Reactor reduced to 10°C; HRT reduced from 18 to 9 hours
February 2015	323	Switched to real PE wastewater feed
March 2015	366	Removal of membrane unit
April 2015	366-383	Sedimentation and filtration testing
April 5, 2015	383	Reactor taken out of service

From day 150 to day 323, the average SCOD of synthetic influent was 245 ± 63 mg/L. Data prior to day 150 was not utilized due to the artificially high standard deviation discussed in Section 3.5.1. The average SCOD concentration of the real PE

influent was 130 ± 57 mg/L. Over the course of the entire project, the SCOD concentration in the reactor averaged 42 ± 19 mg/L.

SCOD can be used as an indicator of process function, but should not be utilized to attempt a mass balance. This is due to the difficulty in calculating or measuring the amount of SCOD generated through hydrolysis. SCOD entering the system can be reliably measured, but the entering concentration is not simply reduced through the treatment process. During treatment, bacteria take in substrate and excrete wastes, all of which can affect the SCOD concentration. Additionally, particulate COD in the influent is hydrolyzed to SCOD, increasing the SCOD concentration concurrent to reduction by biological activity. Mass balance analysis is very difficult using SCOD due to the complex nature of SCOD generation and removal during treatment. Although a mass balance is not advised, SCOD concentration is an indicator of the health of an anaerobic process because VFAs are included in the SCOD measurement. The reactor performed well, producing average SCOD removal of 75% throughout the project. Low VFA concentrations in conjunction with biogas production indicate that the microbial community was active and converting soluble substrate into biomass and methane.

As seen in Figure 4.1, permeate SCOD concentration was similar to the SCOD concentration in the reactor vessel, indicating the COD exclusion by membrane filtration was not removing a significant portion of SCOD. Therefore, biological removal of SCOD was the main pathway of removal for soluble compounds. Removal by biological consumption was expected to be the major removal mechanism since the membranes utilized do not remove oxygen demanding soluble compounds like VFAs. In order for these substances to be removed from solution, they must be utilized by the microbial

community. Typical biological degradation pathways in anaerobic systems are methane generation, sulfate reduction and biomass synthesis (Rittman and McCarty, 2001)

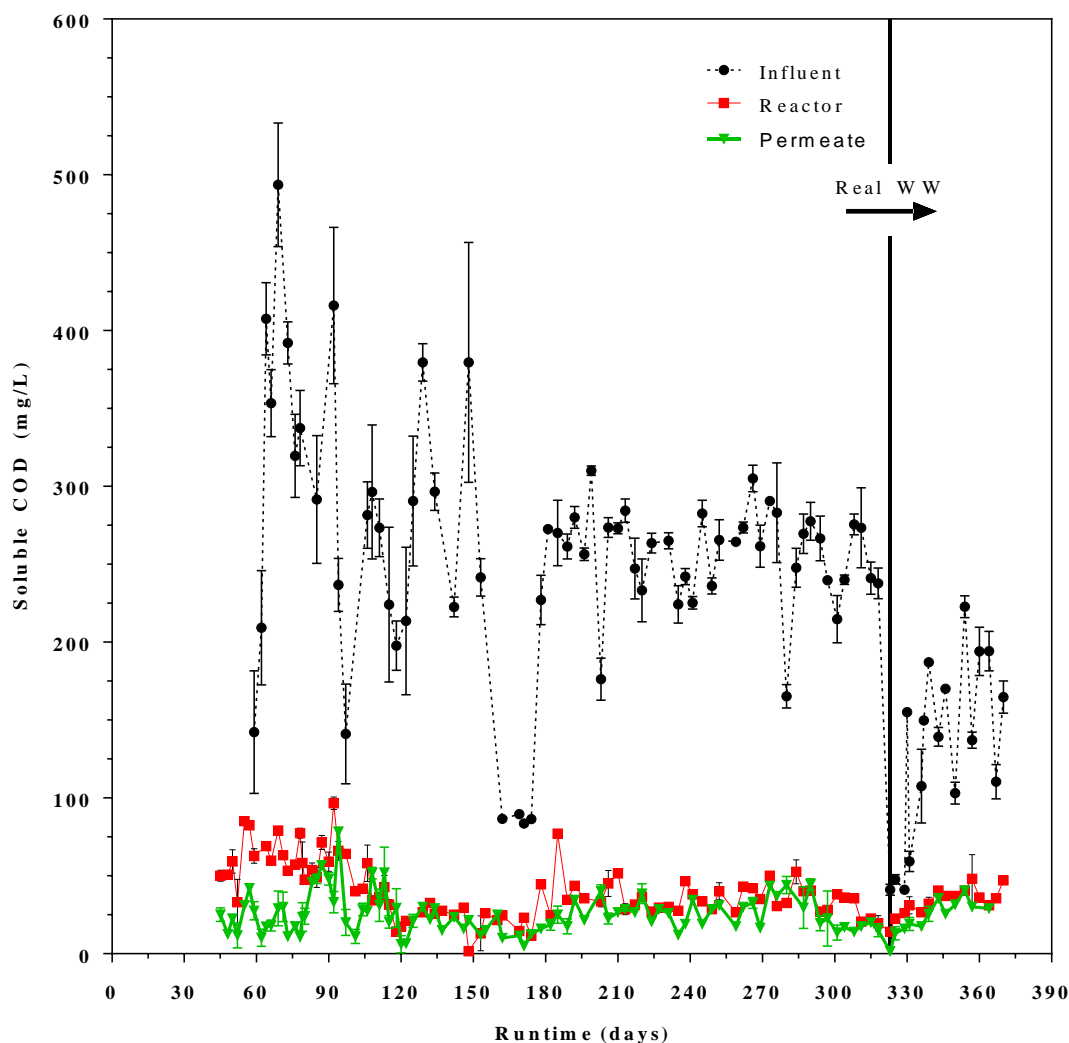


Figure 4.1: Influent, reactor, and permeate SCOD concentrations during operation. Values represent average of triplicate values ± 1 standard deviation.

In addition to SCOD, pH is an important indicator of process health and stability. A statistically significant increase in reactor pH occurred after switching to real PE feed on Day 323, as the average reactor pH increased to 7.15 ± 0.04 from 6.9 ± 0.1 ($p < 0.0001$). Synthetic influent had an average pH of 7.6 ± 0.2 (Days 0-323). Real PE, used from Day

323 to completion of the project, had an average pH of 7.16 ± 0.3 . Despite the change in pH following influent change, reactor pH was within the typical boundaries for methanogen tolerance (pH 6.5-7.6) throughout the project.

VFA concentrations were low throughout the project, and made up the majority of the COD detected. VFA concentrations were converted and expressed as a total COD influence based on stoichiometric requirements for oxidation of each acid, shown in Figure 4.2. This simplification allows for a simpler plot, showing only the impact that VFAs had on overall COD concentration. Throughout the project, VFAs made up an average of 63% of the total effluent SCOD.

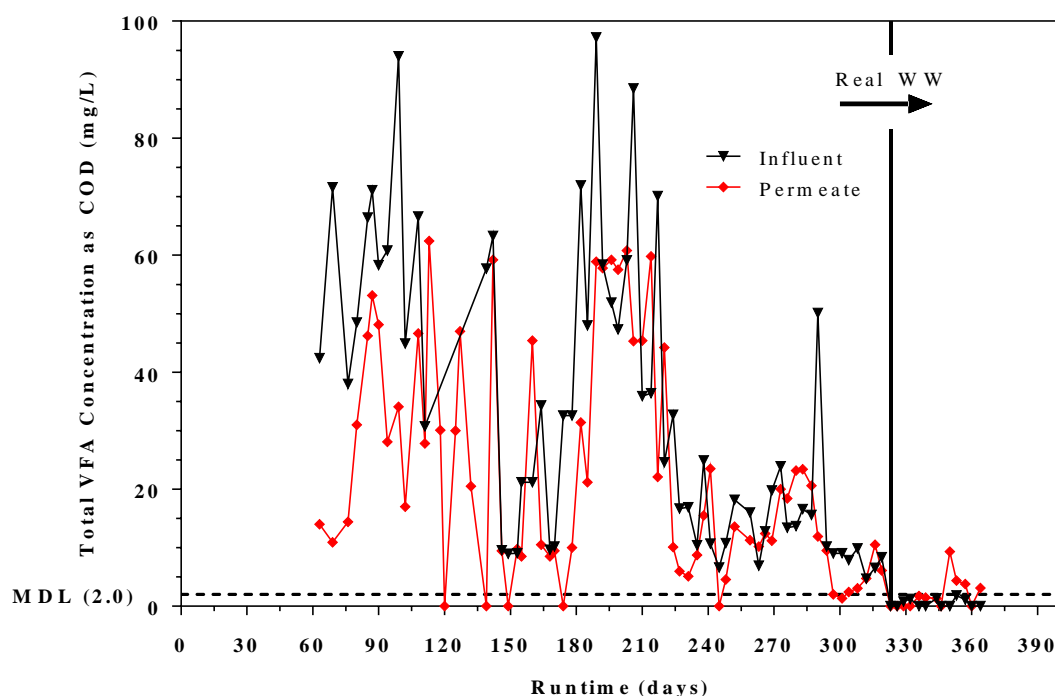


Figure 4.2: VFA concentration (as mg COD/L) of influent and permeate throughout the project.

Importantly, the permeate VFA as COD concentration was very similar to that of the influent and sometimes higher. This phenomena requires analysis of the production of VFAs in the reactor, as the longer chain VFAs contribute more COD than acetate. Also, acetate is directly consumed in the production of methane, and should be at a relatively low concentration if methanogenesis is occurring.

Only acetate was added to the synthetic feed, with no other VFAs developing until acidogenesis occurred in the reactor. The influent VFA concentrations were relatively low throughout the project, with the exception acetic and propionic acids. After switching to real wastewater, propionic acid was present in the influent at around 10 mg/L.

Longer VFAs were formed in the reactor compartment, but were mostly limited to acetic, propionic, butyric, and iso-valyric acids. The concentrations of these compounds were relatively constant below 10 mg/L. Routine below-detection reads (≤ 2 mg/L) of all acids were common throughout the project for all samples in both the reactor contents and permeate. Below-detectable amounts of all acids were common in the influent after switching to real PE. Acetate concentrations in the reactor compartment were lower than influent, indicating biological treatment as the main removal mechanism for acetate. This was expected as the anaerobic community utilized acetate for synthesis and methane production.

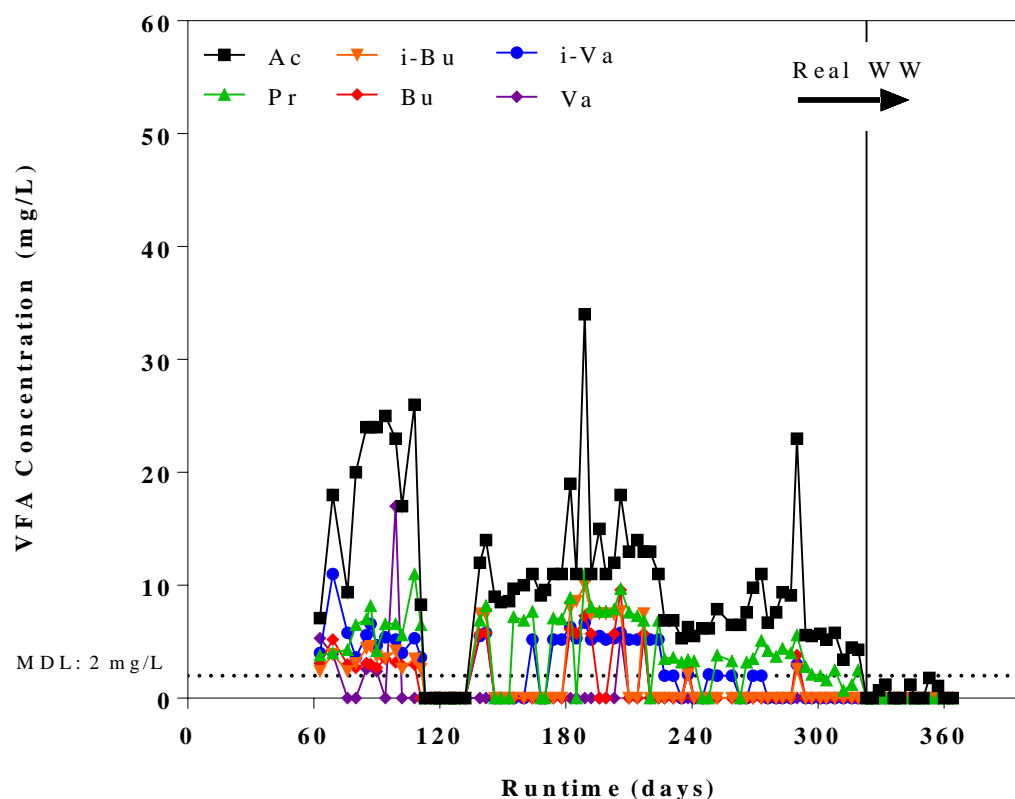


Figure 4.3: Reactor VFA concentrations through the project. Values represent single measurements.

Permeate VFA concentrations remained low throughout the project, never exceeding 25 mg/L for any of the individual VFAs tested. Acetate was the most prevalent of the group, remaining near 10 mg/L throughout the project with a maximum of 22 mg/L. Relative to traditional digesters, the VFA concentrations measured were very low. Typical anaerobic digesters can have VFA concentrations over 100 times higher, with process instability expected at around 1000 mg/L acetate or a propionate to acetate ratio of more than 1.4 (Franke-Whittle et al., 2014). Neither of these conditions were reported throughout the project, indicating that the anaerobic process was very stable.

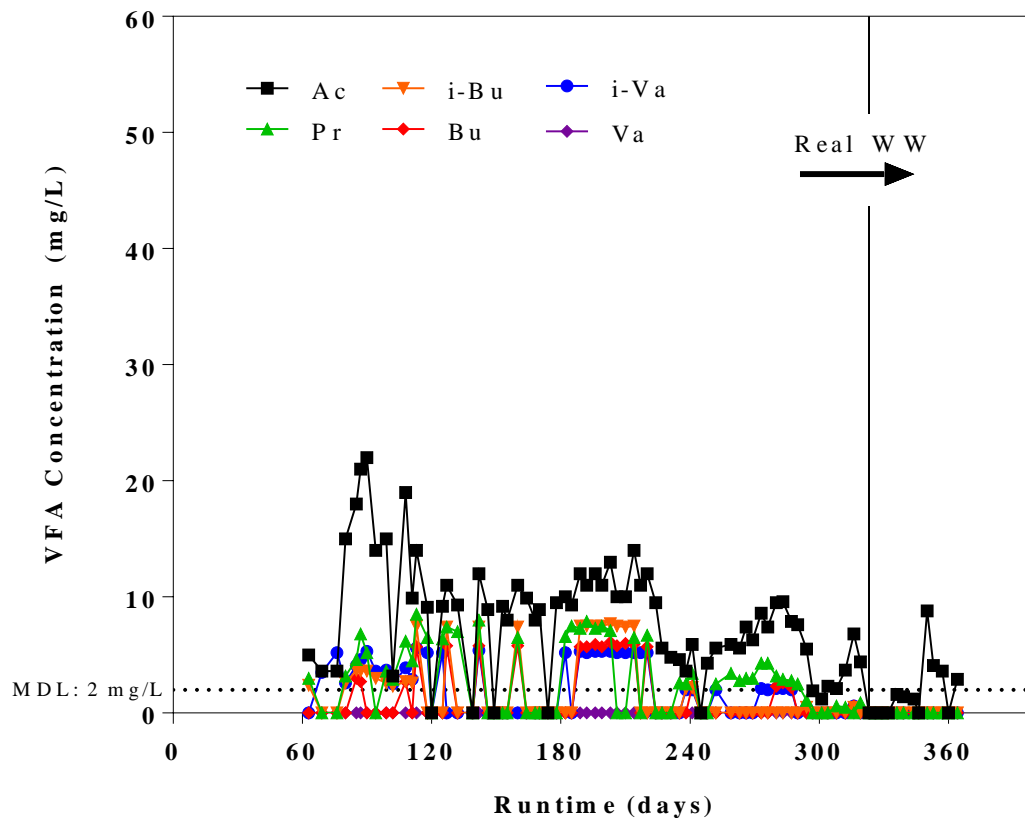


Figure 4.4: Permeate VFA concentrations throughout the project. Values represent single measurements.

In addition to reactor pH, SCOD, and VFA concentration in the reactor effluent, biogas quality was measured following startup and acclimation to cold temperature. A stable anaerobic treatment process can be judged by its methane content in the biogas. A traditional anaerobic digester that is functioning well will have methane content around 50 to 70% in the headspace gas (Speece, 2008). As shown below in Figure 4.5, methane content in the biogas was regularly at or above 60% while feeding synthetic wastewater. After switching to real PE, methane content dropped to about 45% while the biomass acclimated to the new feed source. Additional runtime is required to determine if methane content would return to levels seen prior to switching to real PE.

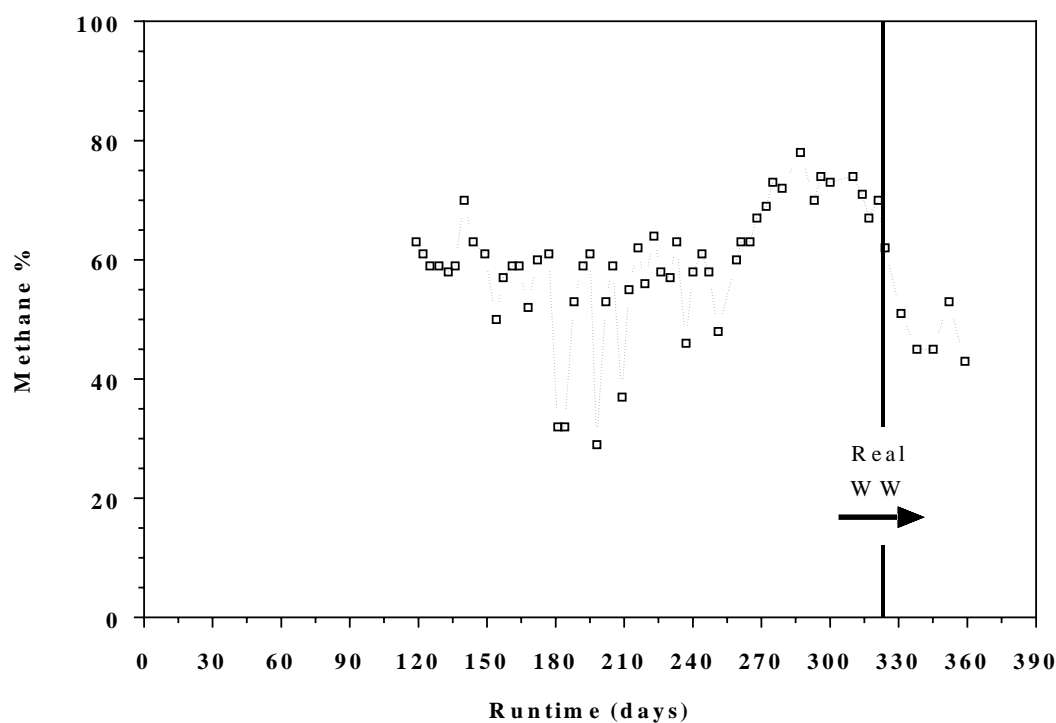


Figure 4.5: Biogas quality indicated by methane content throughout project. Values represent single measurements.

4.2 Coagulant Evaluation and Testing

4.2.1 Optimum pH Determination

Both alum (as aluminum sulfate) and ferric chloride were evaluated for efficacy in treating anaerobic effluent derived from real PE. Effluent from the reactor was first treated by an arbitrary trial dose of 20 mg/L coagulant. Using this dose, pH was varied to investigate the potential benefits of adjusting pH. Preliminary testing suggested ferric chloride to be more effective than alum with regards to producing a readily settled floc. Therefore, pH changes were targeted from 7.5 to 10 to target the optimum pH for ferric hydroxide precipitation (pH 8) (Reynolds and Richards, 1996). Additionally, ferric chloride precipitation requires less alkalinity than alum precipitation, on a mole by mole basis. Ferric chloride uses half the alkalinity that alum requires based only on chemistry (Reynolds and Richards, 1996).

Results from pH variation testing are shown in Figure 4.6 and Figure 4.7. Samples were checked for turbidity after 10 minutes, 30 minutes and 60 minutes of undisturbed settling.

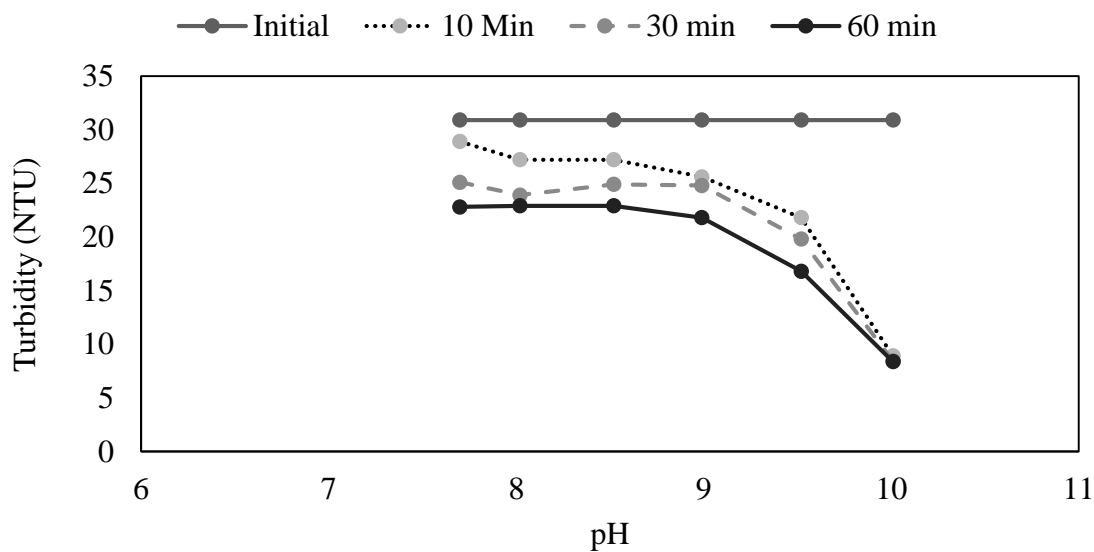


Figure 4.6: Turbidity of supernatant with constant 20 mg/L dose of alum and variable pH. Values represent single turbidity measurements.

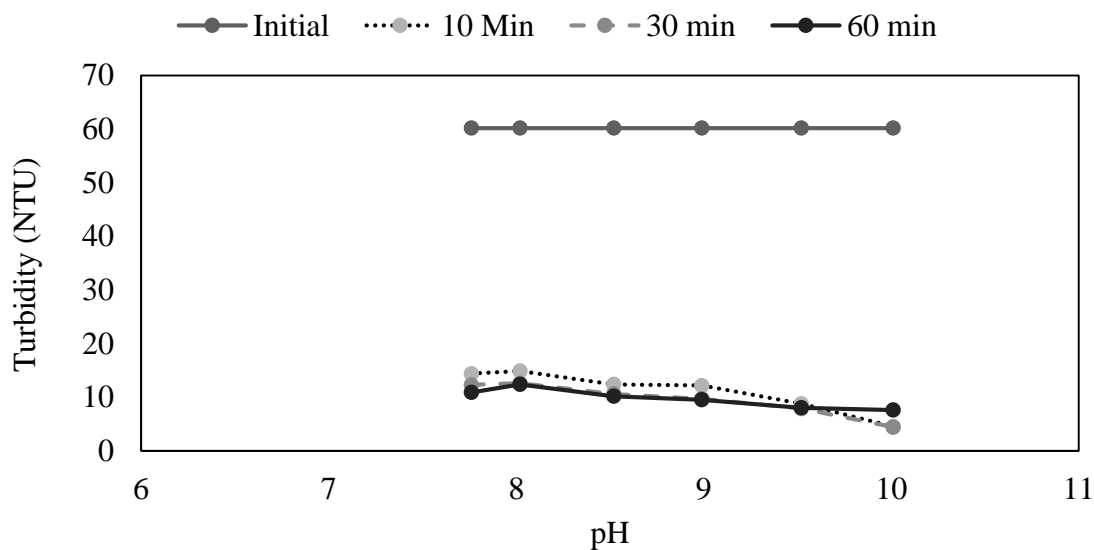


Figure 4.7: Supernatant turbidity with 20 mg/L ferric chloride and variable pH. Values represent single turbidity measurements.

Ferric chloride was much more effective than alum with regards to removal of turbidity. Ferric chloride removed 75% turbidity after 10 minutes at pH 7.75, while alum

removed only 7%. In addition to better removal, ferric chloride also removed turbidity to lower final levels (10.9 NTU vs 22.8 NTU). Increasing the settling time from 10 to 30 minutes resulted in about 20% better turbidity removal for both coagulants. About 10% additional removal was seen between 30 and 60 minutes of settling.

Using the estimates above in conjunction with estimated flows for a 100 MGD plant, pH adjustment was ruled to be cost prohibitive. Adjustments would have required significant acid and caustic doses to reach to a useful level indicated in batch tests followed by readjustment prior to discharge from the settling basin. Therefore, all further sedimentation testing was performed at ambient pH following anaerobic treatment. The ambient pH leaving the digester was approximately 7.6 while the reactor was fed real wastewater.

4.2.2 Optimum Dose Determination

Ferric chloride was expected to perform better than alum, because of the close proximity of reactor pH (7.7) to the optimum pH for formation of insoluble ferric hydroxide (~8). To test this hypothesis, removal dose curves were developed for gravity settling, coagulation by a cationic polymer, coagulation using either ferric chloride or alum, and combinations of each. The tested combinations are shown below in Table 4.2.

Table 4.2: Summary of coagulant and polymer combinations used in batch testing

Option	Coagulant	Polymer
1	None	None
2	None	1 mg/L cationic
3	Alum (2-100 mg/L)	None
4	Alum (2-100 mg/L)	1 mg/l cationic
5	Ferric chloride (2-100 mg/L)	None
6	Ferric chloride (2-100 mg/L)	1 mg/L cationic

Option 1 was tested by including blank controls with each series of tests. The blank jar received no chemical coagulant and tested gravity settling as a comparison to the chemical coagulants. Chemical coagulation proved to be beneficial in all subsequent testing, reducing both COD concentration and turbidity as compared to the blank jar. Turbidity was measured at 10, 30 and 60 minutes to develop a settling time profile for the process.

Little change in turbidity occurred between 10 minutes and 60 minutes of settling for all tests, shown below in Figure 4.8 through Figure 4.11. These data suggested that adequate settling may be accomplished in as little as 10 minutes. Reduced settling times, if possible, could reduce required process volumes. Additionally, COD removal increased with increased chemical coagulant dose. Both alum and ferric chloride showed continuous increase in COD removal with increased dose.

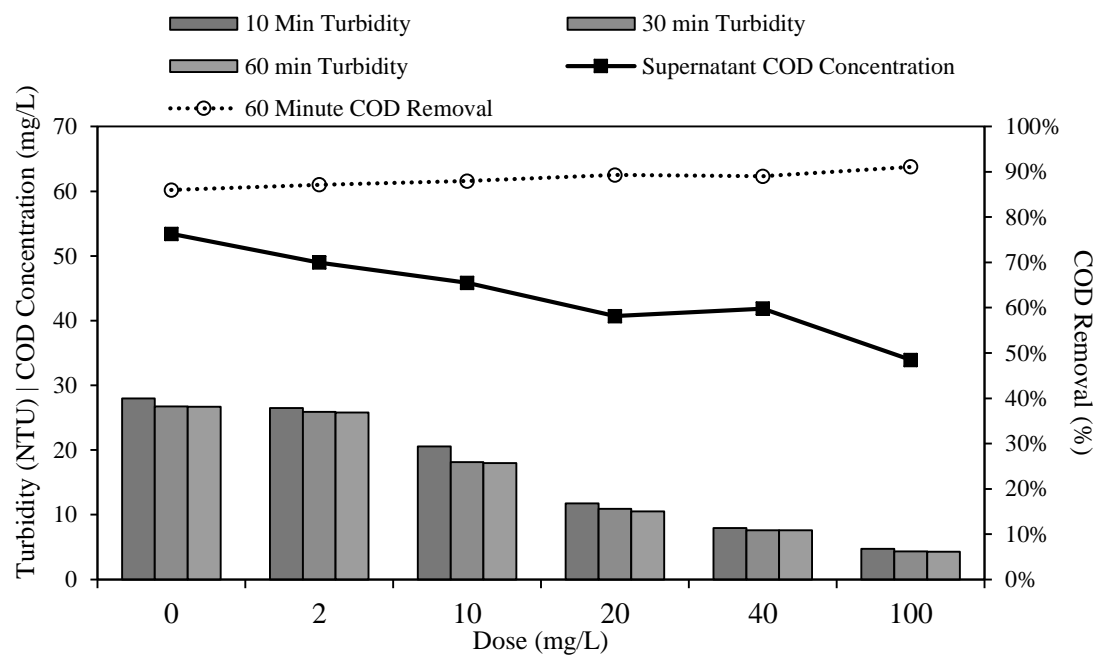


Figure 4.8: Ferric chloride dose comparison at pH 7.75 and influent COD concentration of 381 mg/L. Turbidity measurements are singular values, COD concentration represents the average of duplicate values.

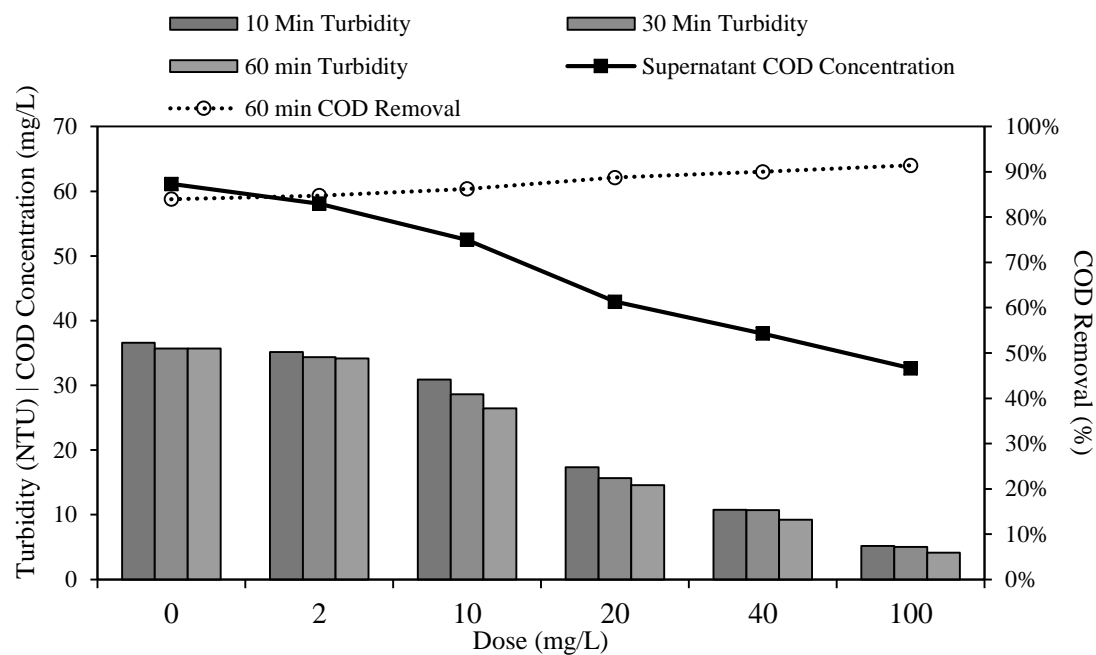


Figure 4.9: Ferric chloride dose comparison with 1 mg/L cationic polymer at pH 7.75 and influent COD of 381 mg/L. Turbidity measurements are singular values, COD concentration represents the average of duplicate values.

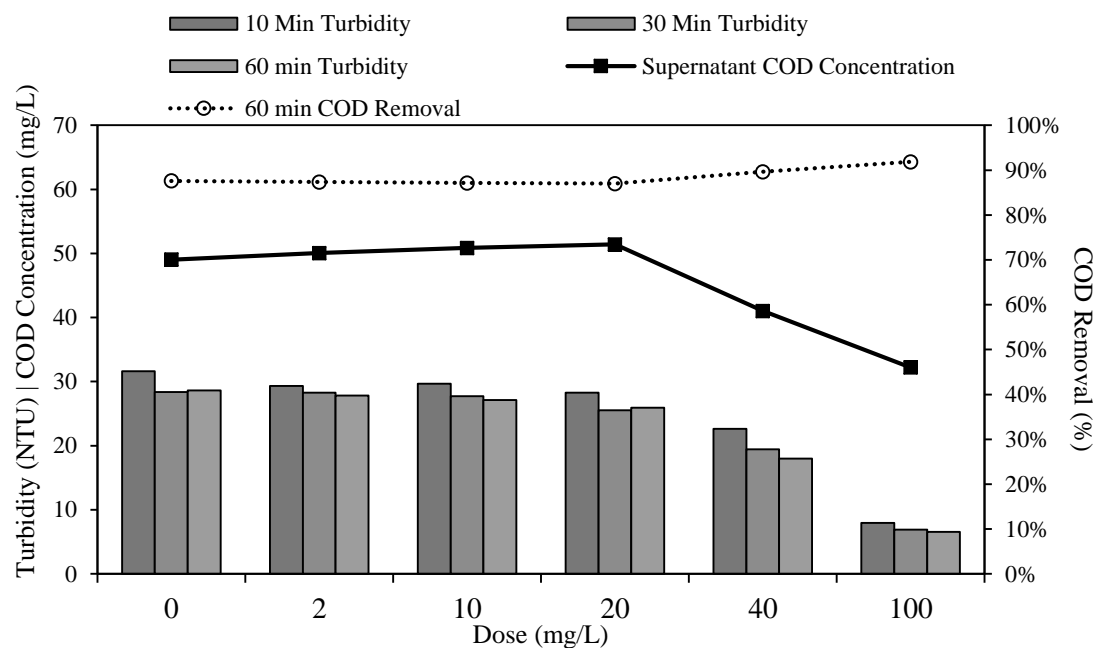


Figure 4.10: Alum dose comparison at pH 7.76 and influent COD of 395 mg/L. Turbidity measurements are singular values, COD concentration represents the average of duplicate values.

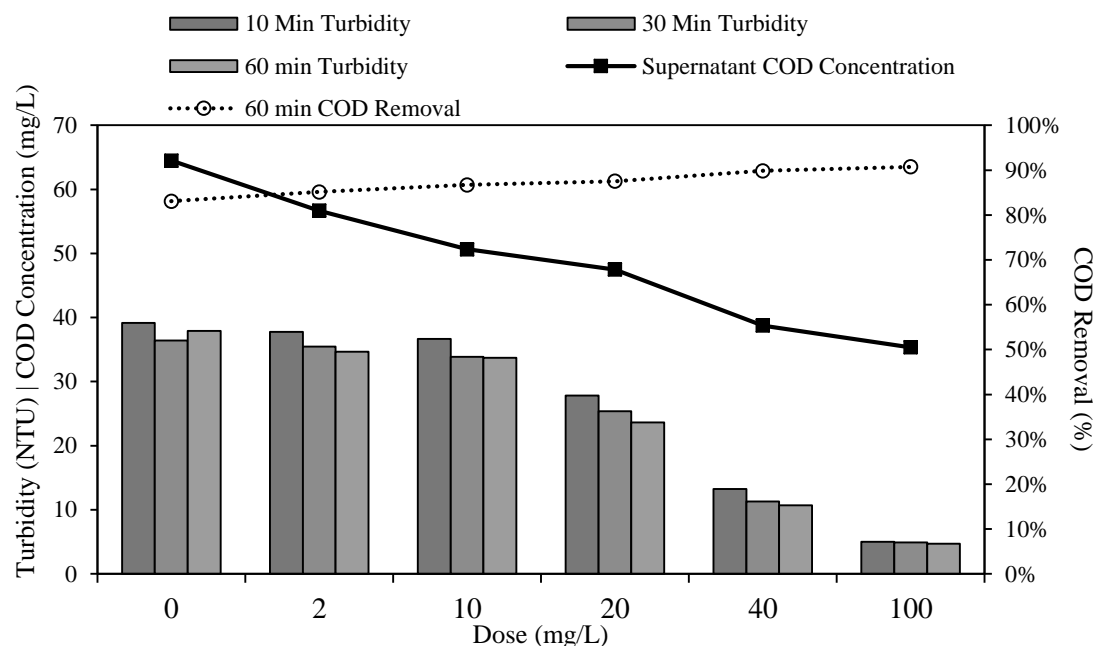


Figure 4.11: Alum dose comparison with 1 mg/L cationic polymer at pH 7.76 and influent COD of 381 mg/L. Turbidity measurements are singular values, COD concentration represents the average of duplicate values.

These data were used to generate a treatment dose curve for each coagulant/polymer combination. These curves were then used to generate a dose required to match the performance of a membrane filtration system.

4.2.3 Establishing an Optimized Coagulant and Dose

Target effluent standards for batch testing were determined using existing membrane filtration data and typical standards given by others (Tchobanoglous et al., 2003). In order to match membrane filtration quality and meet the suggested concentrations, effluent target parameters were set at 10 NTU turbidity and less than 40 mg/L total COD. Using the data generated in batch testing, a dose was selected for each

option in Table 4.2. This dose was estimated to meet the effluent standards suggested above. Doses selected to reach the effluent quality targets are summarized in Table 4.3.

Dose names were shortened in order to easily present the data. Gravity refers to samples settled only by gravity with no chemical coagulants or polymers. The other doses are represented by ferric chloride (F), alum (A), or polymer (P) followed by the dose of each respective chemical. For example, F35P1 refers to a 35 mg/L dose of ferric chloride with 1 mg/L polymer.

Table 4.3: Summary of optimized doses selected for BOD₅ analysis

Option	Description	Shorthand	Concentrations Used
1	Gravity settling only	Gravity	--
2	Polymer only	P1	1 mg/L polymer
3	Alum and polymer	A45P1	45 mg/L alum and 1 mg/L polymer
4	Ferric chloride only	F30	30 mg/L ferric chloride
5	Ferric chloride and polymer	F35P1	35 mg/L ferric chloride and 1 mg/L polymer
6	Alum only	A85	85 mg/L alum

Since the doses in Table 4.3 were estimated, each treatment option was confirmed by a final batch test to establish resulting BOD₅, COD and turbidity concentrations. Results of this final batch test are shown in Figure 4.12. Effluent quality targets are indicated by the horizontal lines at 10 NTU and 40 mg/L COD. Only three coagulant doses met the turbidity criteria: 30 mg/L ferric chloride, 35 mg/L ferric chloride with 1 mg/L polymer, and 85 mg/L alum.

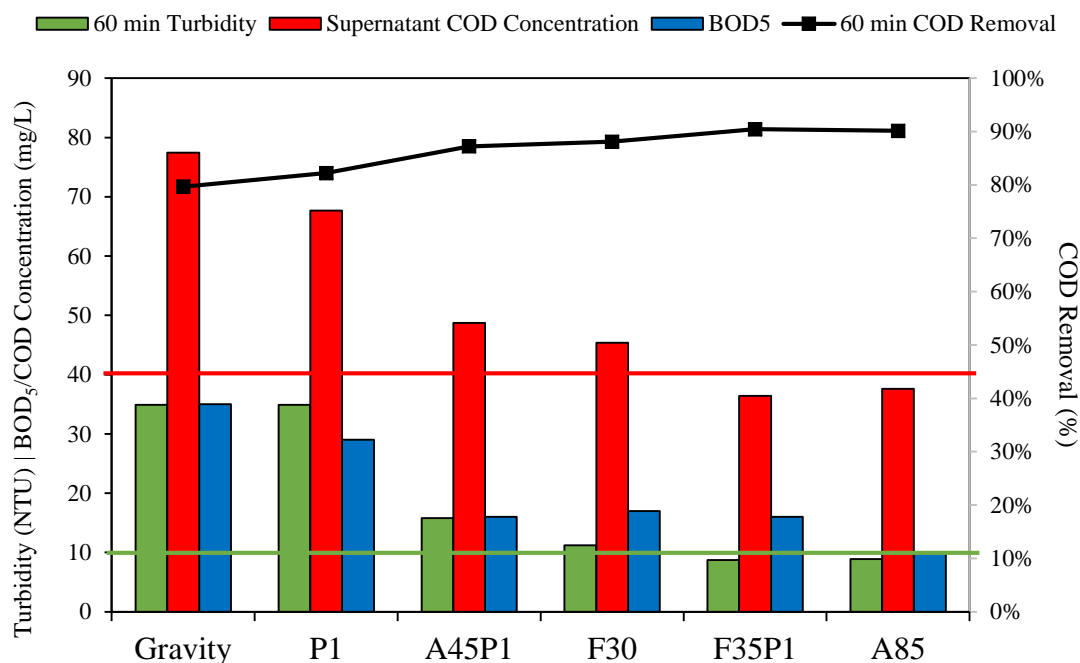


Figure 4.12: Summary of optimized coagulant and polymer doses selected for final testing and evaluation. Initial influent COD was 381 mg/L. Targeted turbidity (10 NTU) appears as the green horizontal line, while targeted COD (40 mg/L) appears as the red horizontal line.

The option with the lowest chemical and clarifier operation cost that was able to meet the targeted discharge concentrations (10 NTU turbidity and around 40 mg/L COD) was a 30 mg/L ferric chloride dose (Figure 4.12). Gravity settling and polymer addition without another coagulant were significantly more cost effective options, but did not produce effluent that met the turbidity and COD criteria. Chemical and clarifier operation costs appear in Table 4.4. Ferric chloride dosed at 30 mg/L was selected as the most cost effective option that met turbidity and COD criteria.

Table 4.4: Summary of treatment costs for optimized coagulant doses. Costs include chemical costs and typical operating costs of secondary clarification at a 100 MGD plant

Option	Chemical and Clarifier Operation Cost (\$/1000 m ³ treated)
Gravity Settling	2.38
P1	2.70
F30	18.41
F35P1	21.30
A45P1	26.35
A85	47.25

4.2.4 Clarification of Anaerobic Effluent using Optimized Coagulant Dose

The optimized dose (30 mg/L FeCl₃) was used to clarify anaerobic effluent for several weeks following removal of the membrane unit. This testing was intended to validate the selected dose by comparing repeated analysis to the predicted COD and turbidity criteria. Producing permit quality effluent using the optimized dose of coagulant was a major goal of the study. Since discharge permits typically regulate BOD₅ in place of COD, it was a priority analysis for clarified effluent. Additionally, COD, SCOD, TSS and VSS were all measured in the supernatant following treatment with ferric chloride and settling by gravity. The results of this analysis appear below.

Supernatant quality was well below typical permit requirements (30 mg/L BOD₅ and TSS), but was higher than that obtained during membrane filtration. Both methods were shown to consistently generate permit quality effluent, indicating that cost effectiveness and ease of use would be main contributors to implementation of one technology over another.

Life cycle analysis, especially if conducted at a level that includes production of the source raw materials to create the chemical coagulants, may yield more representative conclusions as to which chemical coagulant is best in terms of both price and environmental impact. Simple cost analysis is not always representative of the inputs required to produce a product. While the costs of production are always passed along to the purchaser, unseen costs such as pollution, trucking, or non-renewable inputs may go unnoticed.

More batch testing including more precise doses (1 mg/L increments vs 10 mg/L) and combinations with other polymer types and doses could more precisely optimize the coagulant dose. Combined with LCA analysis, the refined doses could be reevaluated to determine the most economical or environmentally friendly option. Complete optimization of the coagulant dose was not in the scope of this work, which represented an attempt to clarify anaerobic effluent to permit discharge quality.

4.2.5 Effluent Quality with Various Clarification Techniques

Days 300-323 were used to compare reactor operation and permeate quality from membrane filtration to effluent produced by alternative clarification techniques. This time period was utilized as the final month of operation prior to switching to real wastewater. The reactor was assumed to be in full-steady state operation and treatment would be as effective as possible.

As shown in Figure 4.13, effluent COD increased following the introduction of real wastewater to the reactor. Prior to the introduction of real wastewater, COD was below 20 mg/L, with BOD₅ less than 10 mg/L. Influent COD and BOD₅ dropped dramatically with the first batch of wastewater gathered due to a dilute batch of PE

gathered at the treatment plant. Subsequent samplings were more indicative of the typical flow seen to the plant.

Enhanced sedimentation produced effluent with similar quality to that of membrane permeate, as indicated in Figure 4.13 and Figure 4.14. A small sample set was split for clarification by membrane filtration or enhanced sedimentation. This separation technique was equally effective at removing COD and BOD₅, but did not remove as much TSS or VSS as membrane filtration (Figure 4.15 and Figure 4.16).

Overall treatment efficiency for COD and BOD₅ was very good, averaging COD removals of 94% for synthetic wastewater and 91% for real wastewater. BOD₅ removal averaged 96% for synthetic and 97% for real wastewater. Following refrigeration and HRT reduction to 9 hours, permeate BOD₅ never exceeded 30 mg/L and was routinely below 10 mg/L. Enhanced sedimentation produced results similar to membrane filtration, with average BOD₅ removal of 92%.

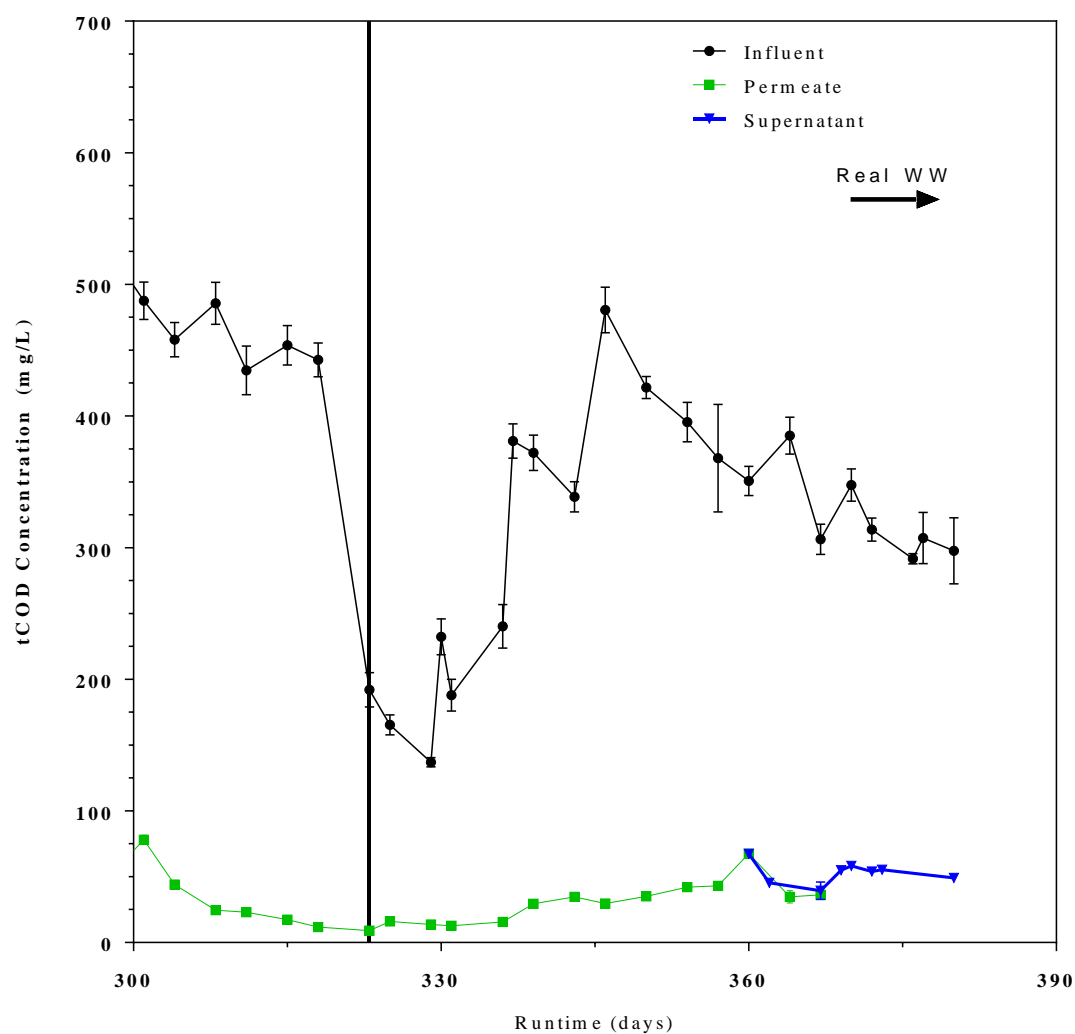


Figure 4.13: Total COD (tCOD) concentration of influent, permeate and supernatant 30 days prior to and after switching feed to real wastewater. Supernatant was treated with 30mg/L ferric chloride and settled for 60 minutes. Values represent average of triplicate values ± 1 standard deviation.

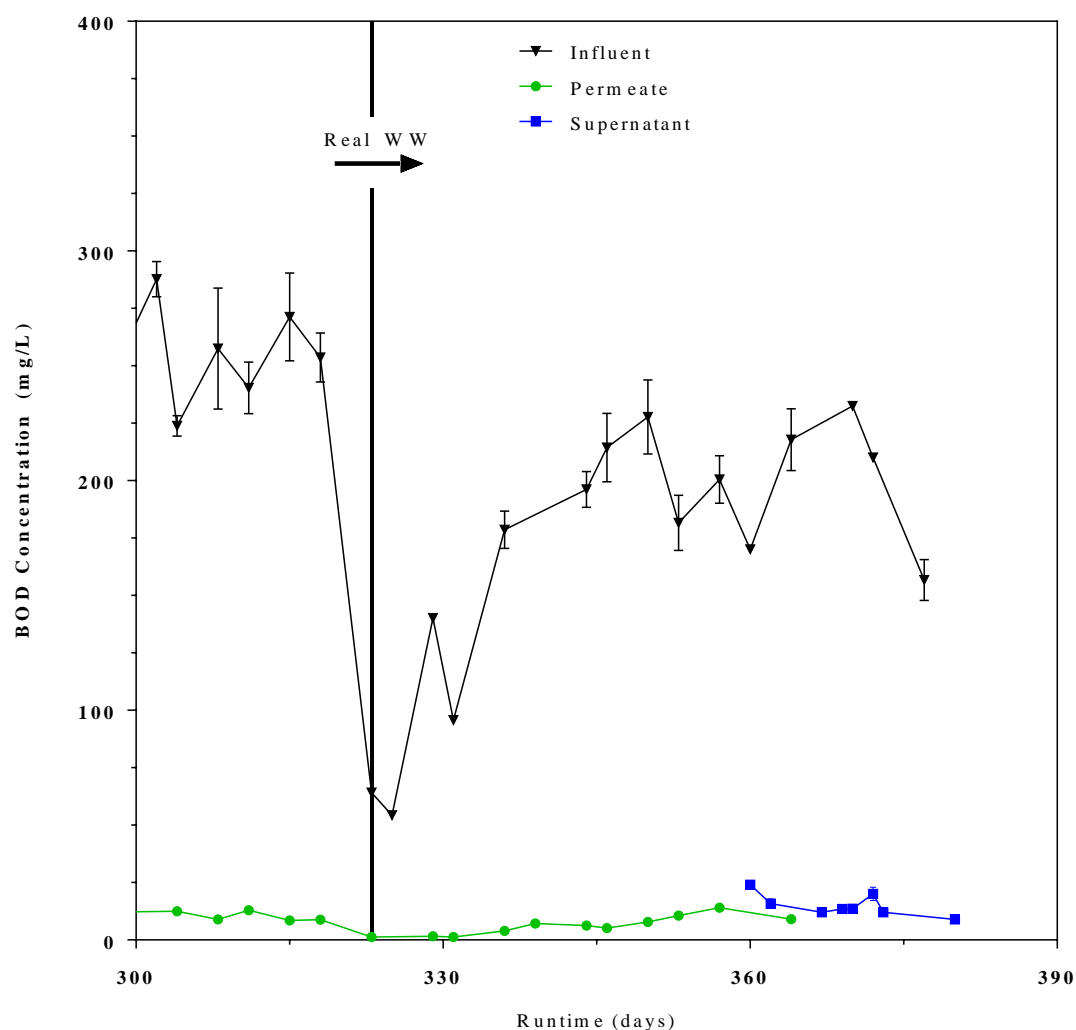


Figure 4.14: Total BOD₅ concentration of influent, permeate, and supernatant 30 days prior to and following switching to real wastewater. Supernatant was treated with 30mg/L ferric chloride and settled for 60 minutes. Values represent average of triplicate analysis ± 1 standard deviation.

Additional removal of solids may have been possible with better optimized settling and chemical dose rates, but would not likely ever reach the same removal levels as filtration. Despite the reduced efficiency, enhanced sedimentation was able to routinely meet typical minimum permit requirements of <30 mg/L TSS, with an average effluent concentration of 14 ± 2 mg/L.

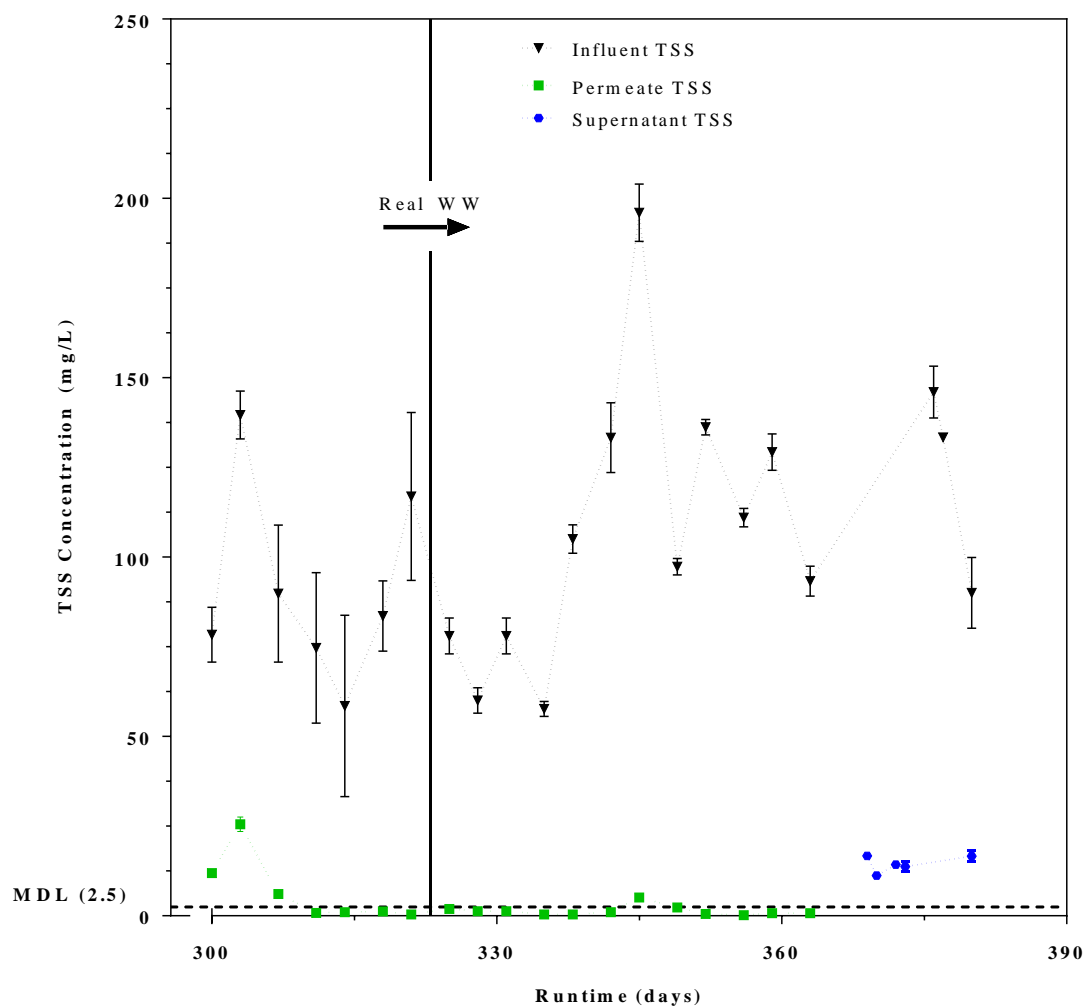


Figure 4.15: TSS concentrations of influent, permeate, and supernatant from Day 300 to end of project. Supernatant was treated with 30mg/L ferric chloride and settled for 60 minutes. Values represent average of triplicate analysis ± 1 standard deviation.

Permeate TSS and VSS concentrations were very low throughout the project aside from a peak around day 300. This peak was determined to be a membrane failure, which was addressed at around day 310. Following corrective action with the membrane, permeate quality quickly returned to levels near or below the minimum detection limit of 2.5 mg/L. VSS made up about 80% of the TSS, which was in line with the suggestion

that VSS make up 60-80% of the total dry solids in primary sludge or waste activated sludge (Speece, 2008).

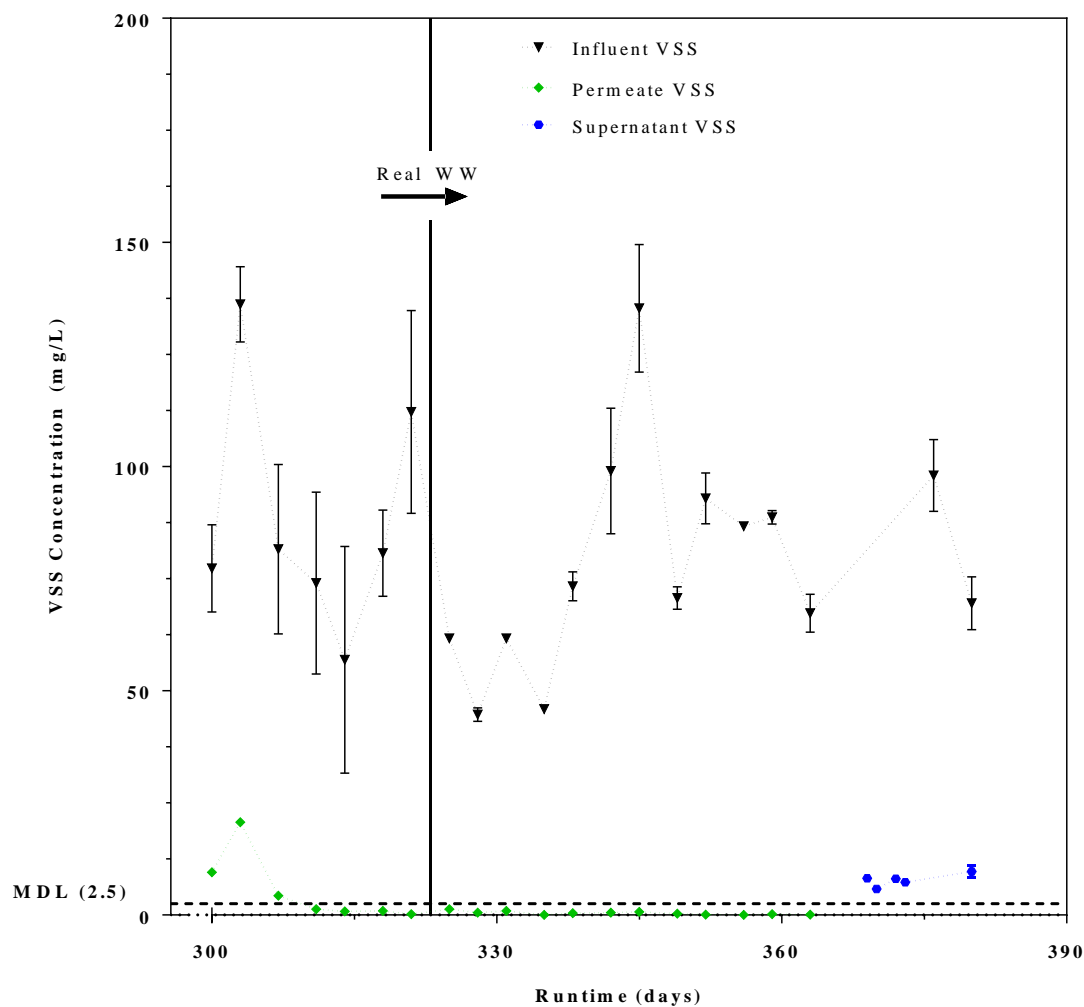


Figure 4.16: VSS concentrations of influent, permeate, and supernatant from Day 300 to end of project. Supernatant was treated with 30mg/L ferric chloride and settled for 60 minutes. Values represent average of triplicate values ± 1 standard deviation.

4.2.6 Clarification with Alternate Technologies

In addition to membrane filtration and enhanced sedimentation, two other clarification techniques were tested: filtration with a proprietary cloth media and

electrocoagulation. Tests of these techniques were preliminary, and were not optimized for effectiveness or cost. Analysis results were compared to membrane filtration and enhanced sedimentation, as shown in Table 4.5.

Table 4.5: Performance and cost data for all clarification techniques utilized while treating real PE. Results indicate average values plus/minus one standard deviation (where shown). Values with no standard deviation represent a singular result.

Parameter (mg/L or as listed)	Membrane Filtration	Enhanced Sedimentation	Cloth Filtration	Electrocoagulation
Final BOD ₅ (mg/L)	6.5±4.2	14 ± 5	20	< 30
Final COD (mg/L)	37±14	53 ± 9	60 ± 12	58 ± 2
Final SCOD (mg/L)	23±10	32 ± 9	46 ± 15	26 ± 2
Final TSS (mg/L)	Below Detection	15 ± 3	62	124 ± 8
Final VSS (mg/L)	Below Detection	8 ± 2	Not tested	78 ± 3
Chemical and operating cost (\$ per 1000 m ³ treated)	~\$30	~\$18	Unknown	>> \$1000

Analysis using the cloth media required high sample volumes (~20 L), making collection difficult due to the scale of the reactor system (3.2 L total volume). Therefore, only a single sample was analyzed for BOD₅ and TSS.

Results of the single test indicated that cloth media filtration was able to reduce BOD₅ to a concentration less than 30 mg/L. Despite the reduction in BOD₅, TSS

concentration was well above permit requirements. In order to develop this technology for application to anaerobic effluent clarification, more suspended solids must be removed from the liquid stream, possibly by adding coagulants.

Electrocoagulation produced an effluent with acceptable BOD but with very high TSS concentrations. This was attributed to the development of flocs that were large, but semi-buoyant. These flocs were not readily settled, but did not float on the surface either. This produced a difficult separation situation for traditional settling operations. The flotation layer was too low to be removed from the top of a sedimentation tank, but did not settle well enough to avoid inclusion with the extraction of effluent.

Membrane filtration consistently produced the highest quality effluent with regards to both BOD₅ and TSS relative to the clarification techniques tested in this work. Enhanced sedimentation was able to produce effluent near that quality, but at an anticipated price lower than membrane filtration. Anticipated costs for membrane filtration range greatly, but unpublished analysis of this system estimates energy consumption at 0.30 kWh per m³ treated (Seib et al., 2015). This energy usage was estimated to be an average value in the range of potential energy consumption by a fluidized bed reactor system equipped with an external, crossflow membrane. The range of values for energy consumption was estimated between 0.10 and 0.50 kWh per m³ treated. Using the average equated to an estimated treatment cost of \$30 per 1000 m³ treated. This value includes only the cost of treatment, excluding operational costs for cleaning and maintenance. Therefore, the likely cost of operation for a membrane filtration unit is higher.

The optimized dose for chemical coagulation was estimated at about \$16 per 1000 m³ treated. Previous work estimated secondary clarification energy consumption at about 20000 kWh per day at a 100 MGD plant utilizing aerobic secondary treatment (Newell et al., 2012). Assuming similar operational characteristics with anaerobic effluent as aerobic effluent, daily flow of 100 MGD and an electricity cost of \$0.045/kWh, this translates to an operational cost of \$2.38 per 1000 m³ treated. Addition of the chemical costs to an average value for existing secondary treatment yields a total treatment cost of about \$18.38 per 1000 m³ treated. At a facility treating 100 MGD, this equates to a daily cost of about \$7000, excluding sludge disposal.

Interestingly, COD and BOD₅ were relatively easy to remove without filtration using very small pore openings. Enhanced sedimentation achieved BOD₅ removal above 90% without any filtration, while membrane filtration provided BOD₅ removal only slightly better but at increased operation costs. This occurrence was also shown with filtration through the cloth media.

The cloth media also yielded a 90% decrease in BOD₅ across the filter, which had a nominal pore size opening of 10 µm. Viewed in conjunction with the unfiltered supernatant and membrane permeate, COD size distribution appeared to be an important characteristic to evaluate for COD removal capabilities. Removal of only relatively large particles resulted in greatly decreased BOD₅ concentrations, implying that membrane ultrafiltration may not be required. Potentially, filtration using larger openings could produce permit quality effluent, with less energy costs than that of membranes with smaller openings. Further investigation of the size distribution of organics in the wastewater was explored by sequential membrane filtration.

4.3 Wastewater COD Characteristics

Characterization of the size distribution of the constituents of the PE used in this project was determined to be a valuable area of research. Size distribution of the bulk organic content was measured by sequential filtration with analysis by COD.

4.3.1 Wastewater Size Distribution

Sequential filtering of raw PE showed no significant difference in COD concentration of PE between 1.2 microns and 3 microns. In fact, the COD concentration at 0.22 microns was less than 15% different than 1.2 microns for trial 1 and only 10% lower for trial 2, as shown in Figure 4.17. These relatively small differences indicated that the majority of the COD in a sample was larger than 3 microns or smaller than 0.22 microns. COD larger than 3 microns can likely be settled or filtered easily and COD smaller than 0.22 microns is assumed to be soluble and removed by biological activity.

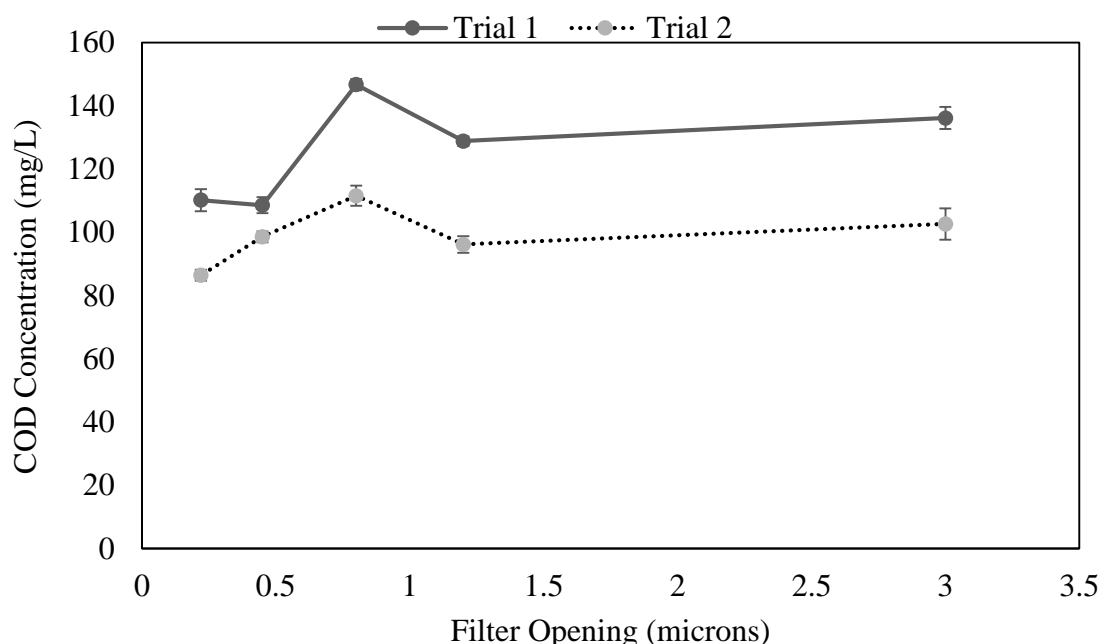


Figure 4.17: COD distribution in two untreated PE samples. Unfiltered COD for Trial 1 and 2 was 350 mg/L and 280 mg/L, respectively.

Filtration tests shown in Figure 4.17 began with COD concentrations of 350 and 280 mg/L, respectively. Filtrate from the 3 micron filter had a COD concentration of approximately 60% of the PE influent. Therefore, only 40% of COD in the sample was smaller than 3 microns. Additionally, filtration through a 0.22 micron filter produced filtrate with a COD concentration of about 30% of the influent. Therefore, about 10% of the total COD in either trial was between 0.22 and 3 microns in size. Filtration below 3 microns results in little additional COD removal. This data suggests that it may be most beneficial to target COD larger than 3 microns for sedimentation.

Additional testing used anaerobic effluent for COD separation. This testing showed no statistical difference between material filtered through a 3 micron filter or a 0.22 micron filter. Results of this testing are shown in Figure 4.18. Filtration with a 3

micron filter removed 85% of COD in the reactor effluent. Similar removal values were noted at all tested filter openings, indicating that the majority of the COD in the sample was greater than 3 microns. Remaining COD was less than 0.22 microns in diameter. Therefore, it is unlikely that these small particles could be removed by sedimentation.

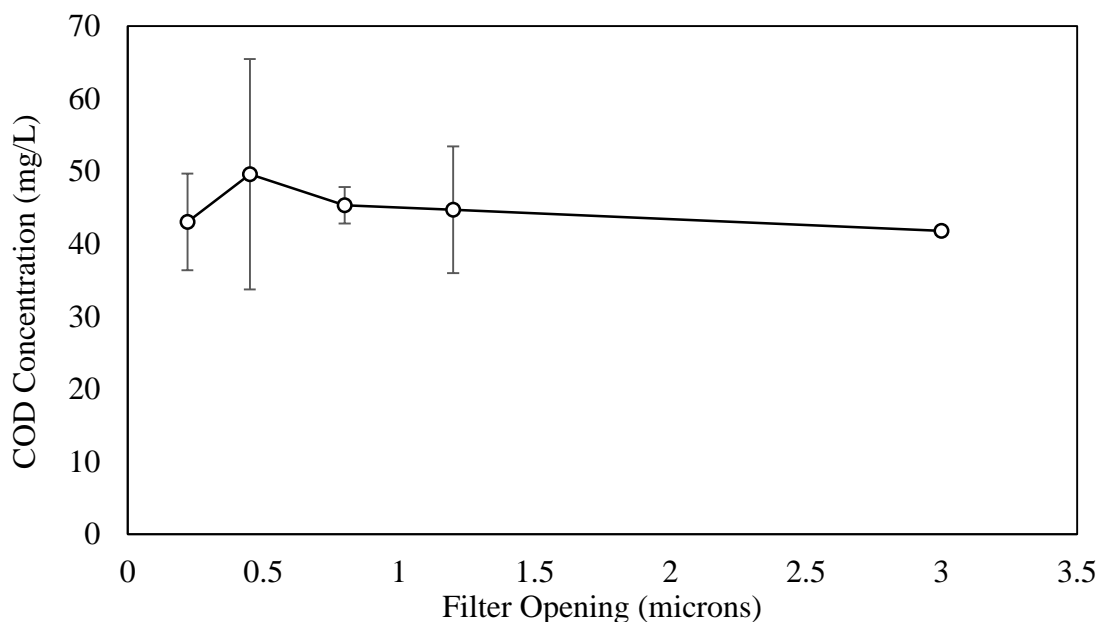


Figure 4.18: Distribution of COD in anaerobic reactor effluent. Initial COD concentration was 280 mg/L. Points represent the average of triplicate COD measurements. Error bars represent one standard deviation.

Comparison of the data in Figure 4.18 with results from membrane filtration showed that permeate from the membrane (nominal pore size of 0.002 microns) had an average total COD of 30 ± 16 mg/L. Membrane filtration showed removal of only 10 mg/L more than the sample filtered through a 3 micron disk filter. With a nominal pore size opening of approximately 0.002 microns, the membrane filter required about 1500 times smaller openings to remove an additional 10 mg/L COD. Smaller pore size openings can translate to higher capital and operational costs by requiring higher TMP to

generate permeate. These data suggest that using membranes with much larger pore sizes may be conducive to producing similar quality effluent at lower cost.

4.3.2 Ratio of BOD₅ to COD

Typical raw municipal wastewater ratio of BOD₅ to COD (BCR) is approximately 0.5 to 0.6 (Tchobanoglous et al., 2003). Significant differences in BCR were noted when comparing influent, reactor effluent, permeate and supernatant. Values, along with sample sizes used to generate these values appear below.

Table 4.6: Ratio of BOD₅ to COD at various points in the treatment process. BCR values represent the average of the sample set plus/minus one standard deviation.

Type of Wastewater	Sample Size	BCR
Raw PE	64	0.50 ± 0.08
Anaerobic Effluent	8	0.40 ± 0.14
Permeate	62	0.34 ± 0.16
Supernatant from Enhanced Sedimentation	8	0.26 ± 0.07

BCR decreased throughout the treatment process, with statistically significant differences between PE and anaerobic effluent BCR values ($p=0.0034$) and anaerobic effluent and supernatant BCR values ($p=0.024$). There was no statistical difference between anaerobic effluent and permeate or permeate and supernatant BCR values.

An extremely statistically significant difference in BCR existed between both the raw PE and permeate, and raw PE and supernatant ($p < 0.0001$). Estimation of BOD₅ by COD testing must take into account differences in these ratios. Implementation of a membrane or sedimentation process may depend on anticipated removal values for BOD₅. These values are often estimated by COD, due to relative ease of COD testing. If an inaccurate BCR is assumed, project efficiency or viability may be adversely affected.

5 CONCLUSIONS

5.1 Reactor Operation

The fluidized bed reactor performed well throughout the project, indicating that it would be a good reactor configuration to apply to low strength municipal wastewater at low temperature. Startup was achieved relatively quickly, with stable performance within 60 days of initial seeding. The initial seeding sources were presumed to have started a culture well suited to the feedstock and temperature at which the reactor was operated. The initial HRT was lowered from 18 hours to 9 hours and the operating temperature was lowered from ambient (approximately 22°C) to 10°C without detriment to the soluble COD concentration in the reactor. Additionally, VFA concentrations remained low and pH was stable, indicating that process performance was acceptable and the microbial community remained active.

Biogas production was consistent, but the setup conditions prohibited complete collection of all biogas generated. These difficulties prevented the completion of a full mass balance based on COD, as a large portion of COD entering the system was not accounted for. Despite the issues collecting biogas, gas that was collected was rich in methane, averaging nearly 60% over the course of the project. Methane concentration in the biogas remained above 40%, even following the abrupt switch to real wastewater feed.

Reactor performance was stable following removal of the membrane system, demonstrating that increased wasting of biomass was not detrimental to the treatment process. Increased wasting of solids without affecting treatment efficiency led to the

belief that not all biomass retained in the system was active. It is important to further investigate the effects of SRT on these systems, both at startup and after maturation.

Overall, anaerobic treatment worked at cold temperatures, even when treating dilute wastewater. Key factors in the system included separation of the SRT and HRT through the use of biomass attachment to media in the form of GAC. In addition to retaining biomass to counteract slow growth rates, it is likely that attached growth media provides an environment that promotes higher mass transfer kinetics. These benefits make the FBR configuration ideal for implementation of anaerobic treatment as an alternative to activated sludge in temperate climates.

5.2 Determination of Optimum Coagulant Dose

Cost analysis showed that pH adjustment for optimization of sedimentation would be cost prohibitive. Therefore, testing was carried out at ambient pH. At this pH, ferric chloride performed better than alum and was selected for further testing. Batch tests conducted using anaerobic effluent and a variety of coagulant doses concluded that a 30 mg/L dose of ferric chloride was optimal to treat fresh, cold anaerobic effluent. This selection was also based on basic cost analysis of chemical prices and clarifier operation. This dose of coagulant was then used to treat anaerobic effluent in an attempt to generate effluent of similar quality to membrane filtration.

Membrane filtration, gravity settling, enhanced sedimentation and alternative clarification methods were effective in reducing effluent TSS and BOD₅ concentrations. Specifically, membrane filtration routinely produced effluent BOD₅ concentrations below 10 mg/L with TSS below the detection limit. Enhanced sedimentation with ferric

chloride (30 mg/L) was also effective in removing BOD₅ and TSS, both of which routinely were below 15 mg/L as measured in the supernatant.

Both cloth filtration and electrocoagulation were tested as alternatives to membrane filtration and chemical coagulation, respectively. Cloth filtration removed BOD₅ to 20 mg/L, but did not meet permit requirements for TSS concentration. Electrocoagulation produced effluent with low BOD₅ (<30 mg/L) without the need for added chemicals, but operational costs were significantly higher than other methods and high solids concentrations were not acceptable.

5.3 COD Distribution in Wastewater

COD in raw PE was found to be mostly in the fractions larger than at least 3 microns and smaller than 0.22 microns. These data suggested that current definition of soluble is rather arbitrary, and could perhaps be redefined to be more definitive with respect to its application. For instance, large particles tend to settle well, so a nominal 1 micron limit for TSS measurements would be a good gross indicator of settling potential and solution clarity. On the other hand, soluble COD is supposed to measure non-particulate COD, but include many biological sources as they are smaller than the 0.45 micron standard filter size.

Exclusion by the membrane rejection was not a major COD removal mechanism, since the COD of the anaerobic effluent showed little difference from that of filtrate utilizing a 3 micron filter. Larger membrane sizes could allow for lower energy and capital costs by lowering the TMP required to produce effluent. In order to maintain effluent discharge regulations, a membrane utilizing pore openings less than 1 micron

would still produce effluent with little or no residual TSS as detected by standard methods.

5.4 Recommendations and Future Research

A fluidized bed reactor coupled with enhanced sedimentation is recommended for further testing at the pilot scale. Enhanced sedimentation is expected to be a viable option for clarification of anaerobic effluent from a FBR treating PE. The data presented suggest that cold temperature anaerobic treatment of dilute wastewater is not only possible with this setup, but could be an alternative to activated sludge.

Further optimization of the chemical coagulants used to treat the anaerobic effluent could further reduce cost. All wastewaters are different, implying that optimization throughout a system's lifetime is necessary to provide optimal financial operation. Deeper analysis of polymer addition may be a low cost option to reduce chemical use, thereby reducing operation costs.

Research into membranes with larger filter openings (0.1 – 1.0 microns) is recommended to develop cost and performance curves for operation of these membranes. The data presented here suggest that these larger openings may provide treatment similar to that of membrane with much smaller pore openings, perhaps at reduced cost. Full life cycle cost analysis is required to determine the most beneficial option for treatment of PE, both financially and environmentally. Financial concerns often drive innovation, but protection of human and environmental health are the main goals of wastewater treatment. Therefore, it is important to conduct analysis regarding not only the operation of wastewater treatment processes, but also the production, transport and disposal of all

inputs and outputs of the process. It is only when these full analyses are conducted that the overall picture of what process is most beneficial can be fully understood.

6 BIBLIOGRAPHY

- APHA, AWWA, WEF, 1999. Standard Methods for the Examination of Water and Wastewater.
- Booker, N.A., Priestley, A.J., Fraser, I.H., 1999. Struvite Formation in Wastewater Treatment Plants: Opportunities for Nutrient Recovery. *Environ. Technol.*
- CIA, 2015. Country Comparison for Electricity Consumption [WWW Document]. World Factb. URL <https://www.cia.gov/library/publications/the-world-factbook/rankorder/2233rank.html> (accessed 5.19.15).
- Connaughton, S., Collins, G., O'Flaherty, V., 2006. Psychrophilic and mesophilic anaerobic digestion of brewery effluent: A comparative study. *Water Res.* 40, 2503–2510.
- Dereli, R.K., Ersahin, M.E., Ozgun, H., Ozturk, I., Jeison, D., van der Zee, F., van Lier, J.B., 2012. Potentials of anaerobic membrane bioreactors to overcome treatment limitations induced by industrial wastewaters. *Bioresour. Technol.* 122, 160–170.
- Doyle, J.D., Parsons, S.A., 2002. Struvite formation, control and recovery. *Water Res.* 36, 3925–3940.
- Draaijer, H., Maas, J.A.W., Schaapman, J.E., Khan, A., 1992. Performance of the 5 MLD UASB Reactor for Sewage Treatment at Kanpur, India.
- Eckenfelder, W.W., Ford, D.L., Engle, A.J., 2009. Industrial Water Quality, 4th ed. McGraw-Hill, New York.
- EPA Office of Water, 2006. Wastewater Management Fact Sheet, Energy Conservation.
- Foresti, E., Zaiat, M., Vallero, M., 2006. Anaerobic processes as the core technology for sustainable domestic wastewater treatment: Consolidated applications, new trends, perspectives, and challenges. *Rev. Environ. Sci. Biotechnol.* 5, 3–19.
- Franke-Whittle, I.H., Walter, A., Ebner, C., Insam, H., 2014. Investigation into the effect of high concentrations of volatile fatty acids in anaerobic digestion on methanogenic communities. *Waste Manag.* 34, 2080–2089.
- Gengec, E., Kobya, M., 2013. Treatment of Baker's Yeast Wastewater by Electrocoagulation and Evaluation of Molecular Weight Distribution with HPSEC. *Sep. Sci. Technol.* 48, 2880 – 2889.
- Heffron, J., 2015. Removal of trace heavy metals from drinking water by electrocoagulation. Marquette University.

- Hu, A.Y., Stuckey, D.C., 2006. Treatment of Dilute Wastewaters Using a Novel Submerged Anaerobic Membrane Bioreactor. *J. Environ. Eng.*
- Huang, Z., Ong, S.L., Ng, H.Y., 2008. Feasibility of submerged anaerobic membrane bioreactor (SAMBR) for treatment of low-strength wastewater. *Water Sci. Technol.* 58, 1925–1931.
- Khoufi, S., Aloui, F., Sayadi, S., 2006. Treatment of olive oil mill wastewater by combined process electro-Fenton reaction and anaerobic digestion. *Water Res.* 40, 2007–16.
- Kim, J., Kim, K., Ye, H., Lee, E., Shin, C., McCarty, P.L., Bae, J., 2011. Anaerobic fluidized bed membrane bioreactor for wastewater treatment. *Environ. Sci. Technol.* 45, 576–581.
- Lettinga, G., Rebac, S., Zeeman, G., 2001. Challenge of psychrophilic anaerobic wastewater treatment. *Trends Biotechnol.* 19, 363–370.
- Lin, H., Chen, J., Wang, F., Ding, L., Hong, H., 2011. Feasibility evaluation of submerged anaerobic membrane bioreactor for municipal secondary wastewater treatment. *Desalination* 280, 120–126.
- Madigan, M., 2012. *Brock Biology of Microorganisms*, 13th edn, International Microbiology.
- McCarty, P.L., Bae, J., Kim, J., 2011. Domestic wastewater treatment as a net energy producer-can this be achieved? *Environ. Sci. Technol.* 45, 7100–7106.
- McCarty, P.L., Smith, D.P., 1986. *Anaerobic Wastewater Treatment*. *Environ. Sci. Technol.*
- Mullen, P., 2015. *Nutrient Recovery from Anaerobic Membrane Bioreactor Permeate Using ion Exchange*. Master's Theses (2009 -).
- Newell, T., Batista, J., Sajjad, A., Johnson, W., 2012. Energy Consumption in Large Wastewater Treatment Plants as a Function of Wastewater Strength.
- NIIR, 2005. *Medical, Municipal and Plastic Waste Management Handbook*.
- Parker, D.S., Barnard, J., Daigger, G.T., Tekippe, R.J., Wahlberg, E.J., 2001. The future of chemically enhanced primary treatment: Evolution not revolution.
- Rebac, S., van Lier, J.B., Lens, P., J.M. Stams, A., Dekkers, F., Th.M. Swinkels, K., Lettinga, G., 1999. Psychrophilic anaerobic treatment of low strength wastewaters. *Water Sci. Technol.* 39, 203–210.

- Reynolds, T.D., Richards, P.A., 1996. Unit Operations and Processes in Environmental Engineering, 2nd ed. International Thomson Publishing, Boston, MA.
- Rittman, B.E., McCarty, P.L., 2001. Environmental Biotechnology: Principles and Applications. McGraw-Hill, New York.
- Seghezzo, L., Zeeman, G., Liel, J.B. Van, Hamelers, H.V.M., Lettinga, G., 1998. A Review : the Anaerobic Treatment of Sewage in UASB and EGSB Reactors. *Bioresour. Technol.* 65, 175–190.
- Seib, M.D., Berg, K.J., Merry, A., Trickle, G., Zitomer, D.H., 2015. Low energy anaerobic membrane bioreactor for domestic wastewater treatment. Milwaukee.
- Shin, C., McCarty, P.L., Kim, J., Bae, J., 2014. Pilot-scale temperate-climate treatment of domestic wastewater with a staged anaerobic fluidized membrane bioreactor (SAF-MBR). *Bioresour. Technol.* 159, 95–103.
- Shu, L., Schneider, P., Jegatheesan, V., Johnson, J., 2006. An economic evaluation of phosphorus recovery as struvite from digester supernatant. *Bioresour. Technol.*
- Skouteris, G., Hermosilla, D., López, P., Negro, C., Blanco, Á., 2012. Anaerobic membrane bioreactors for wastewater treatment: A review. *Chem. Eng. J.* 198-199, 138–148.
- Smith, A.L., Skerlos, S.J., Raskin, L., 2013. Psychrophilic anaerobic membrane bioreactor treatment of domestic wastewater. *Water Res.* 47, 1655–65.
- Smith, A.L., Stadler, L.B., Love, N.G., Skerlos, S.J., Raskin, L., 2012. Perspectives on anaerobic membrane bioreactor treatment of domestic wastewater: a critical review. *Bioresour. Technol.* 122, 149–59.
- Speece, R.E., 1983. Anaerobic biotechnology for industrial wastewater. *Environ. Sci. Technol.* 17, 416A–427A.
- Speece, R.E., 2008. Anaerobic Biotechnology and Odor/Corrosion Control for Municipalities and Industries. Archae Press, Nashville, Tennessee.
- Stuckey, D.C., 2012. Recent developments in anaerobic membrane reactors. *Bioresour. Technol.* 122, 137–48.
- Tchobanoglous, G., Burton, F.L., Stensel, H.D., 2003. Wastewater Engineering, Treatment and Reuse, 4th ed. McGraw-Hill, New York.
- USGS, 2014. Water Questions and Answers [WWW Document]. URL <https://water.usgs.gov/edu/qa-home-percapita.html>

- Williams, A., 2013. Ion Exchange Nutrient Recovery from Municipal Wastewater. Master's Theses (2009 -).
- Wisconsin Public Service, 2015a. Wisconsin Rate Book [WWW Document]. Hist. Wisconsin Electr. Rates. URL http://www.wisconsinpublicservice.com/company/wi_tariffs.aspx
- Wisconsin Public Service, 2015b. Wisconsin Rate Book [WWW Document]. Hist. Wisconsin Gas Rates. URL http://www.wisconsinpublicservice.com/company/wi_tariffs.aspx
- Xu, X., Zhu, X., 2004. Treatment of refractory oily wastewater by electro-coagulation process. *Chemosphere* 56, 889–94.
- Yoo, R.H., Kim, J.H., McCarty, P.L., Bae, J.H., 2014. Effect of temperature on the treatment of domestic wastewater with a staged anaerobic fluidized membrane bioreactor. *Water Sci. Technol.* 69, 1145–50.